Investigating the Excited State Properties of Photoactive TiO_2 Nanoclusters through Non-Adiabatic Molecular Dynamics

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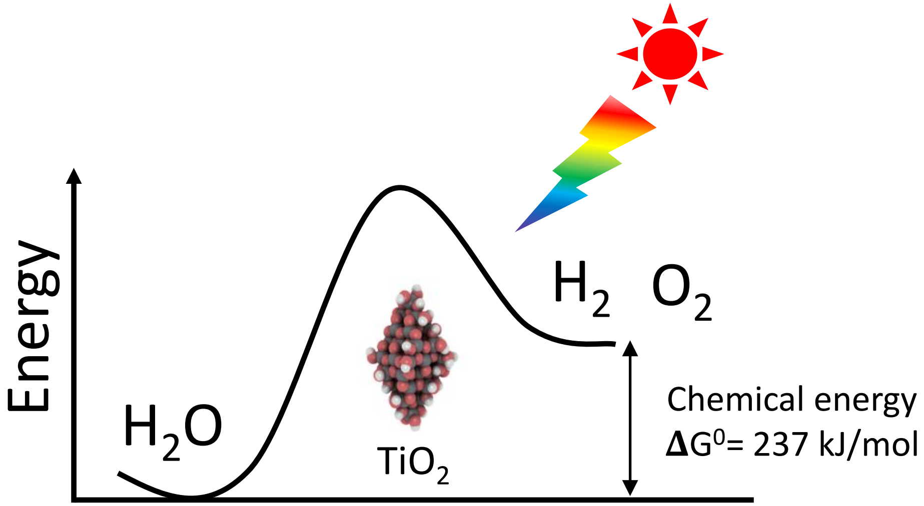
University at Buffalo

OUTLINE

1. Motivation and previous research
2. Methodology - Libra/CP2K workflow
3. First project: role of water and benchmark analysis
4. Second project: recombination or relaxation in small bare NPs
5. Conclusions

Water splitting: a simple idea

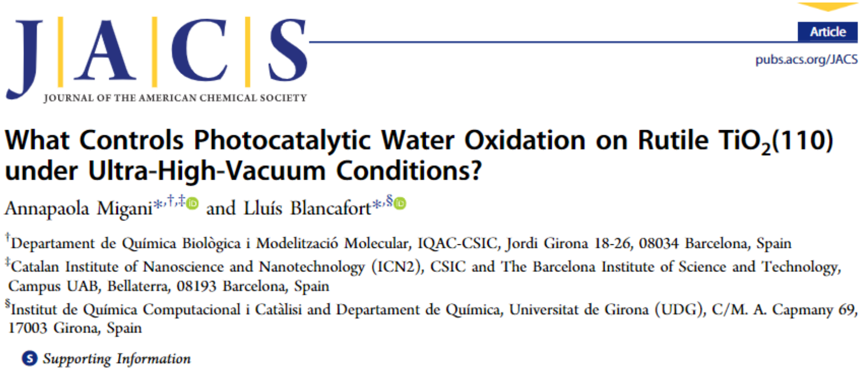
$$H_2O \longrightarrow H_2 + \tfrac{1}{2}\, O_2$$



- Clean energy production but **against** thermodynamics
- Need of external energy -> **photocatalytic water splitting**
- **Anatase titania (TiO_2) nanoparticles** potential solution
- BG is too large. Absorbs only a **small fraction** of solar spectrum.
- It is inert enough, and can be functionalized -> **DSSC**

Previous research

Previous studies based on time-domain version of the Kohn-Sham DFT (KS-DFT):



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Article
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What Controls Photocatalytic Water Oxidation on Rutile TiO_2(110) under Ultra-High-Vacuum Conditions?

Annapaola Migani*[†,‡] and Lluís Blancafort*[§]

[†] Departament de Química Biològica i Modelització Molecular, IQAC-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain
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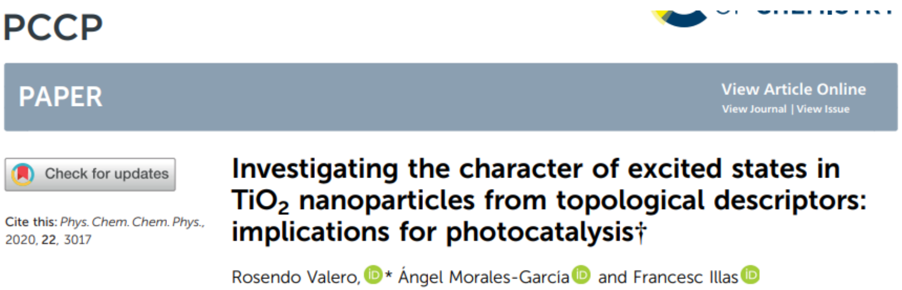
[§] Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona (UDG), C/M. A. Capmany 69, 17003 Girona, Spain

Supporting Information



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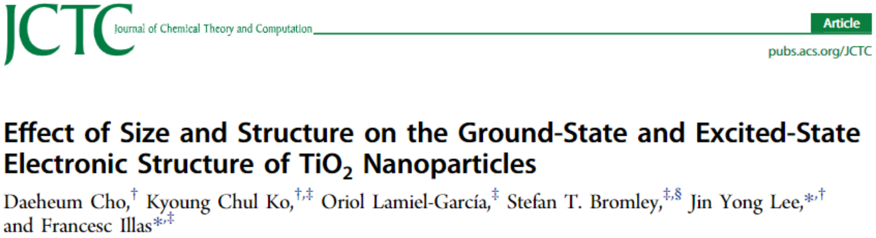
Cite this: *Phys. Chem. Chem. Phys.*, 2020, 22, 3017

Investigating the character of excited states in TiO_2 nanoparticles from topological descriptors: implications for photocatalysis†

Rosendo Valero, * Ángel Morales-García and Francesc Illas



JCTC
Journal of Chemical Theory and Computation

Article
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Effect of Size and Structure on the Ground-State and Excited-State Electronic Structure of TiO_2 Nanoparticles

Daeheum Cho,[†] Kyoung Chul Ko,[†,‡] Oriol Lamiel-García,[‡] Stefan T. Bromley,[‡,§] Jin Yong Lee,*[,†] and Francesc Illas*[,‡]

CHEMICAL REVIEWS

Review
pubs.acs.org/CR

Theoretical Approaches to Excited-State-Related Phenomena in Oxide Surfaces

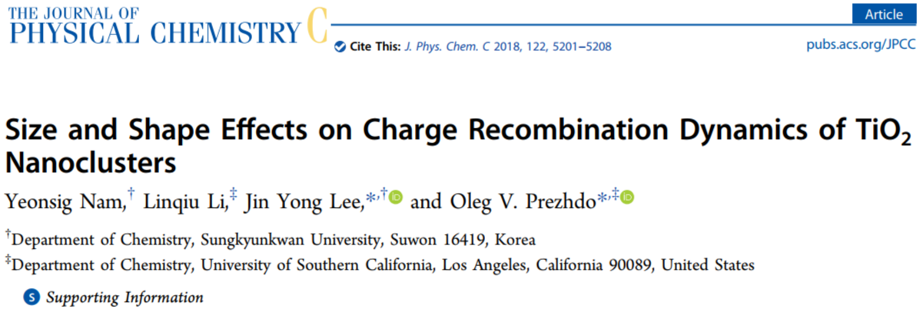
Carmen Sousa,[†] Sergio Tosoni,[†,‡] and Francesc Illas*[,†]

[†] Departament de Química Física and Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, C/Martí i Franquès 1, 08028 Barcelona, Spain
[‡] Departamento de Química, Universidad de Las Palmas de Gran Canaria, Campus Universitario de Tafira, 35017 Las Palmas de Gran Canaria, Spain

A single-particle treatment inadequate for quantitative characterization of the dynamics in systems as TiO_2 nanostructures. More rigorous (linear-response, LR) time-dependent DFT (TD-DFT) framework needed.

Previous research

Non-Adiabatic Molecular NA-MD trusted as the suited technique to investigate the dynamics of excited states


THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

Cite This: *J. Phys. Chem. C* 2018, 122, 5201−5208

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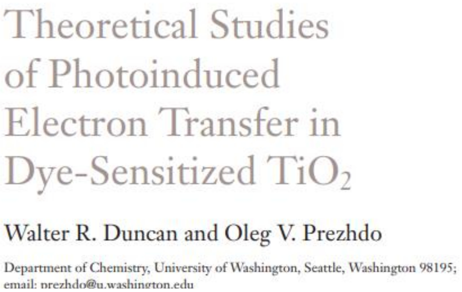
Size and Shape Effects on Charge Recombination Dynamics of TiO_2 Nanoclusters

Yeonsig Nam,[†] Linqiu Li,[‡] Jin Yong Lee,[*,†] and Oleg V. Prezhdo[*,‡]

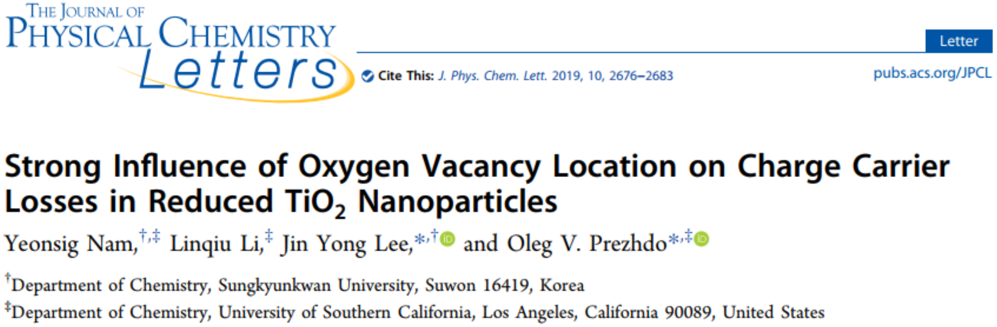
[†]Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea
[‡]Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States

Supporting Information


Theoretical Studies of Photoinduced Electron Transfer in Dye-Sensitized TiO_2

Walter R. Duncan and Oleg V. Prezhdo

Department of Chemistry, University of Washington, Seattle, Washington 98195;
email: prezhdo@u.washington.edu


THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

Cite This: *J. Phys. Chem. Lett.* 2019, 10, 2676−2683

pubs.acs.org/JPCL

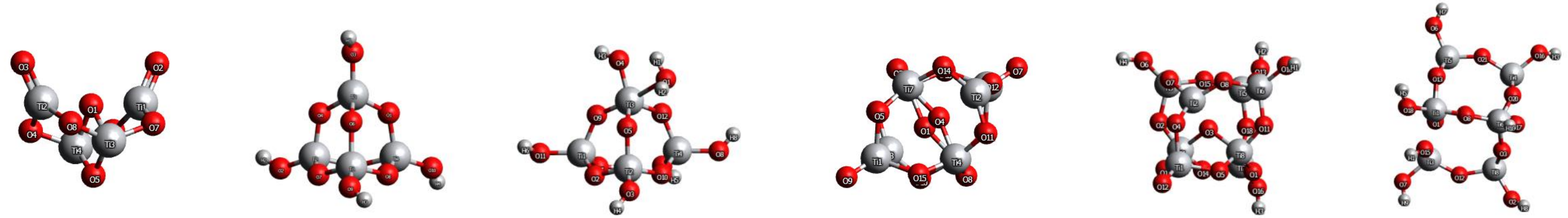
Strong Influence of Oxygen Vacancy Location on Charge Carrier Losses in Reduced TiO_2 Nanoparticles

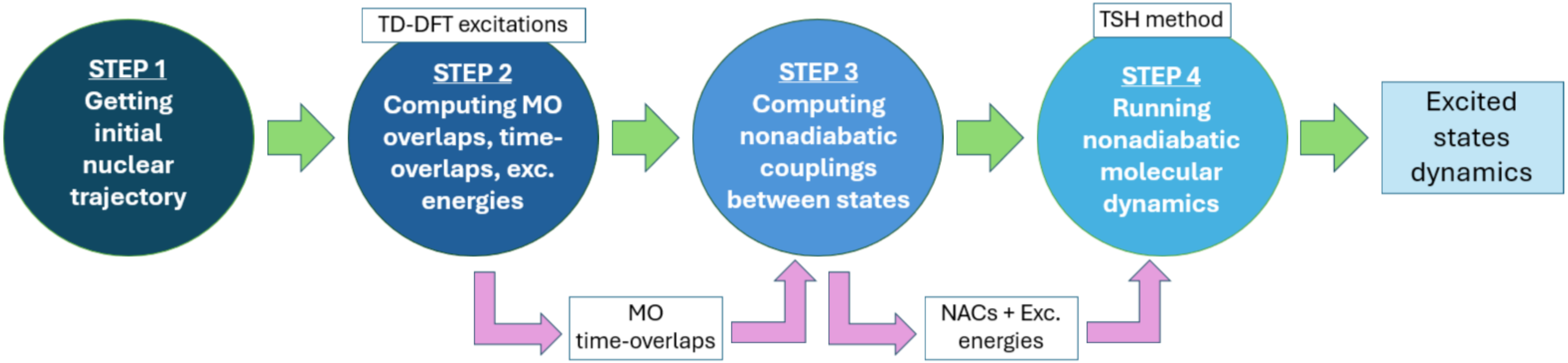
Yeonsig Nam,[†,‡] Linqiu Li,[‡] Jin Yong Lee,[*,†] and Oleg V. Prezhdo[*,‡]

[†]Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea
[‡]Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States

Lack of research concerning the influence of water on photoactive nanostructures when adsorbed in their surfaces

Methodology - Libra/CP2K workflow





TD-DFT excitations

STEP 1
Getting initial nuclear trajectory

STEP 2
Computing MO overlaps, time-overlaps, exc. energies

MO
time-overlaps

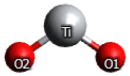
STEP 3
Computing nonadiabatic couplings between states

NACs + Exc.
energies

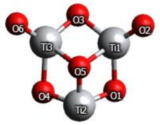
TSH method

STEP 4
Running nonadiabatic molecular dynamics

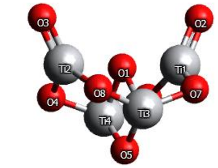
Excited states dynamics



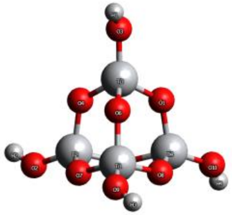
- CP2K: step 1, step 2 (excitations)
- Libra: step 2 (overlaps), step 3, step 4



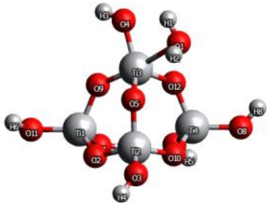
First project: water effect and benchmark analysis



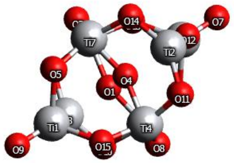
$(TiO_2)_4$



$(TiO_2)_4(H_2O)_2$

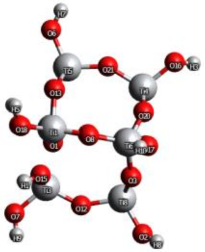


$(TiO_2)_4(H_2O)_4$



$(TiO_2)_8$

$(TiO_2)_8(H_2O)_2$

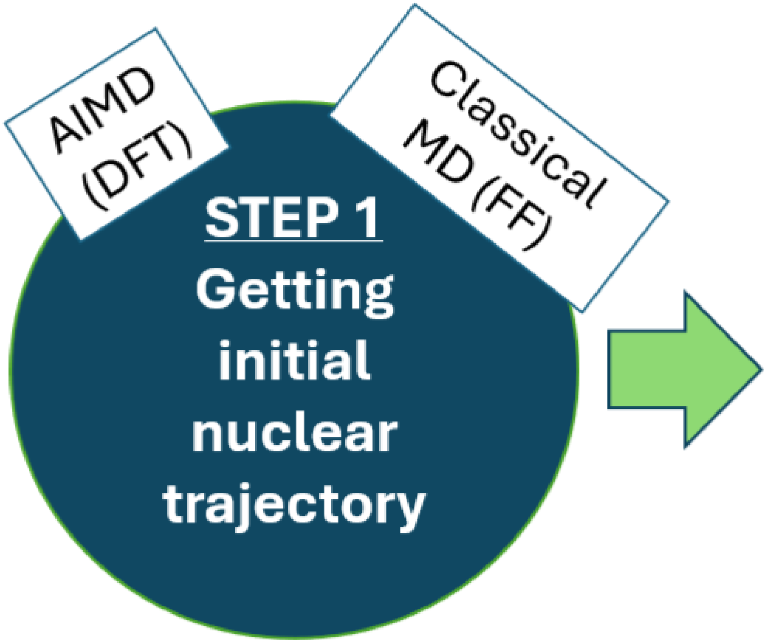


$(TiO_2)_8(H_2O)_5$

Benchmark the used TD-DFT and NA-MD methodologies for their further applications to bigger photoactive nanostructures

Investigate the dependence of static excited state properties and excited state dynamics on the nanocluster size and hydration degree.

First project: water effect and benchmark analysis



GULP: **Classical MD** (NanoTiO & FFTiOH IP)

CP2K: **AIMD (PBE), xTB**

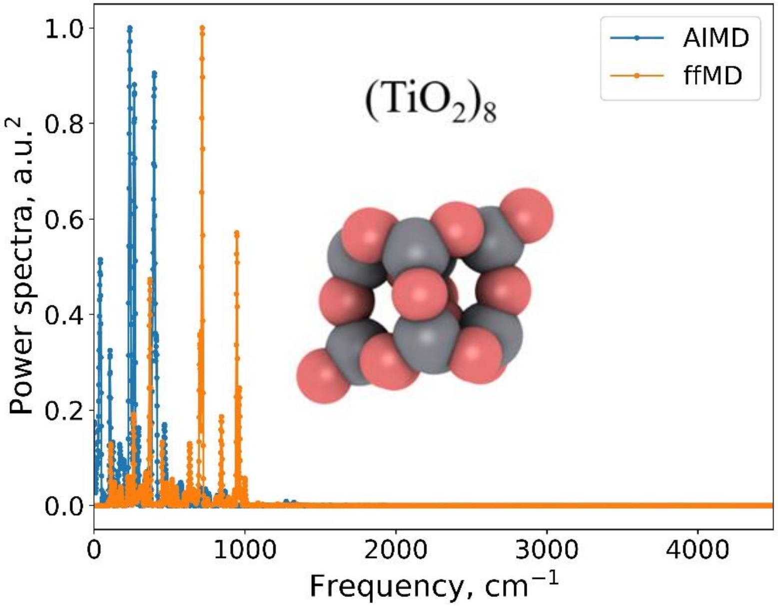
NVT ensemble. Target temperature: 300 K

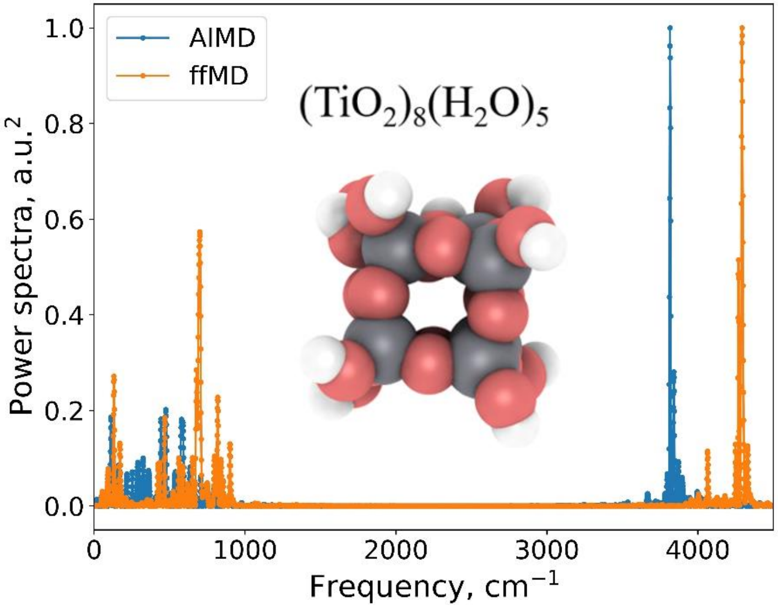
4 ps run (1 ps equilibration + 3 ps production)

1 fs timestep → 3000 different geometries

First project (step I)

The atomic vibrational frequencies of our titania clusters along the 3000 fs runs let us easily compare the performance of either methodology.



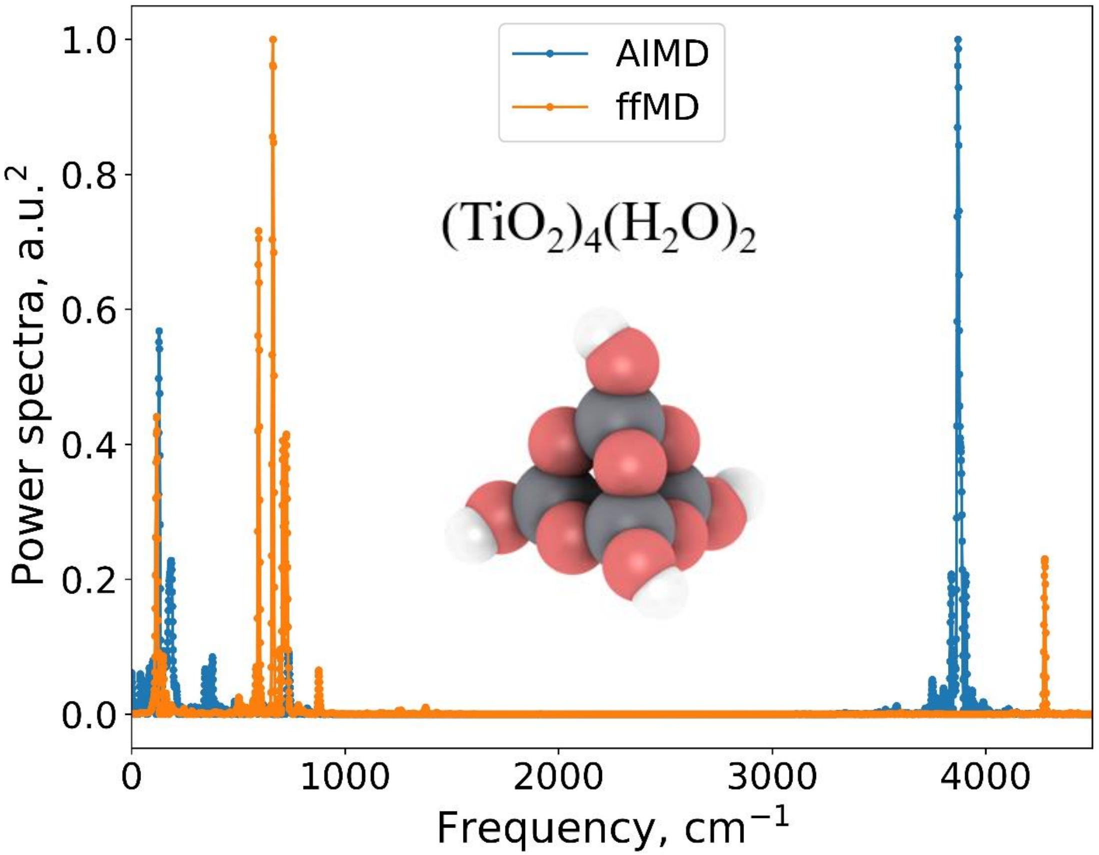


Vib. modes at frequencies similar to those observed in titania bulk phase

100 to 200 cm^{-1} -> Ti-O stretching modes
500-1000 cm^{-1} -> Ti-O-Ti angle bending

Hydrated $(TiO_2)_8$ clusters: characteristic hydroxyl stretching mode around 3700-3900 cm^{-1} values[2]

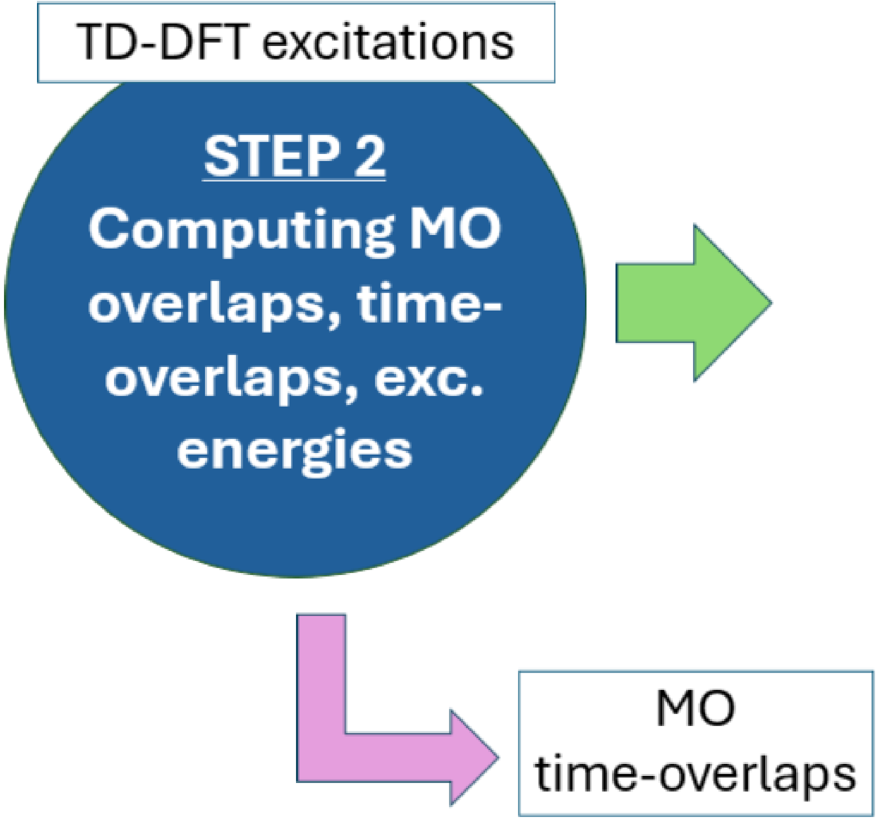
First project (step I)



Anharmonic effects in AIMD approach -> lower frequency values but also busier vibrational densities

Power spectra are qualitatively the same **-> tested FFs are accurate to act as computationally-efficient counterparts to DFT calculations**

First project (step II)



TD-DFT excitations

STEP 2

Computing MO overlaps, time-overlaps, exc. energies

MO time-overlaps

S0 to S1 state transition (but we include up to ten TD-DFT excited states)

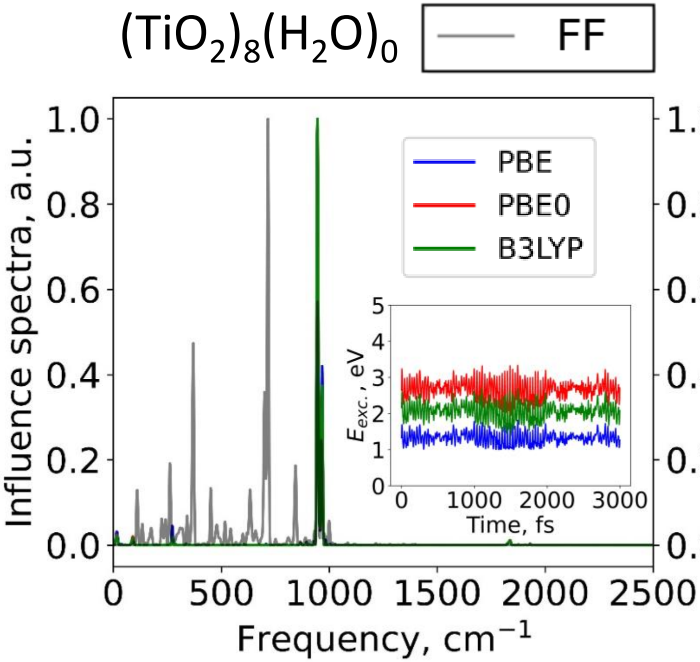
PBE, PBE0 and B3LYP functionals

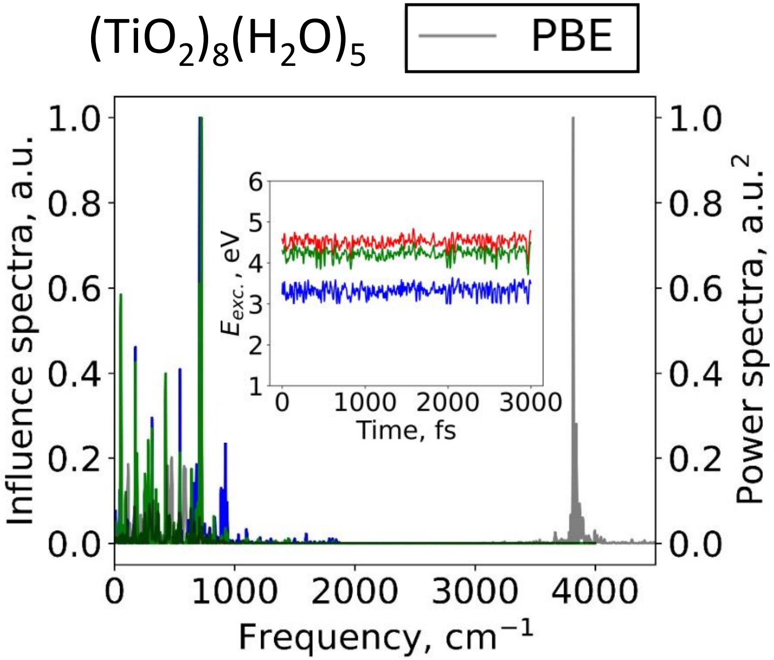
MB representation

Time-overlaps between consecutive geometries, $\langle \Psi_i(t) | \Psi_j(t+\Delta t) \rangle$

First project (step II)

FT of δE_{ij} gives rise to the influence spectra, which shows up the vibrational modes responsible for S0 to S1 transition


$(TiO_2)_8(H_2O)_0$

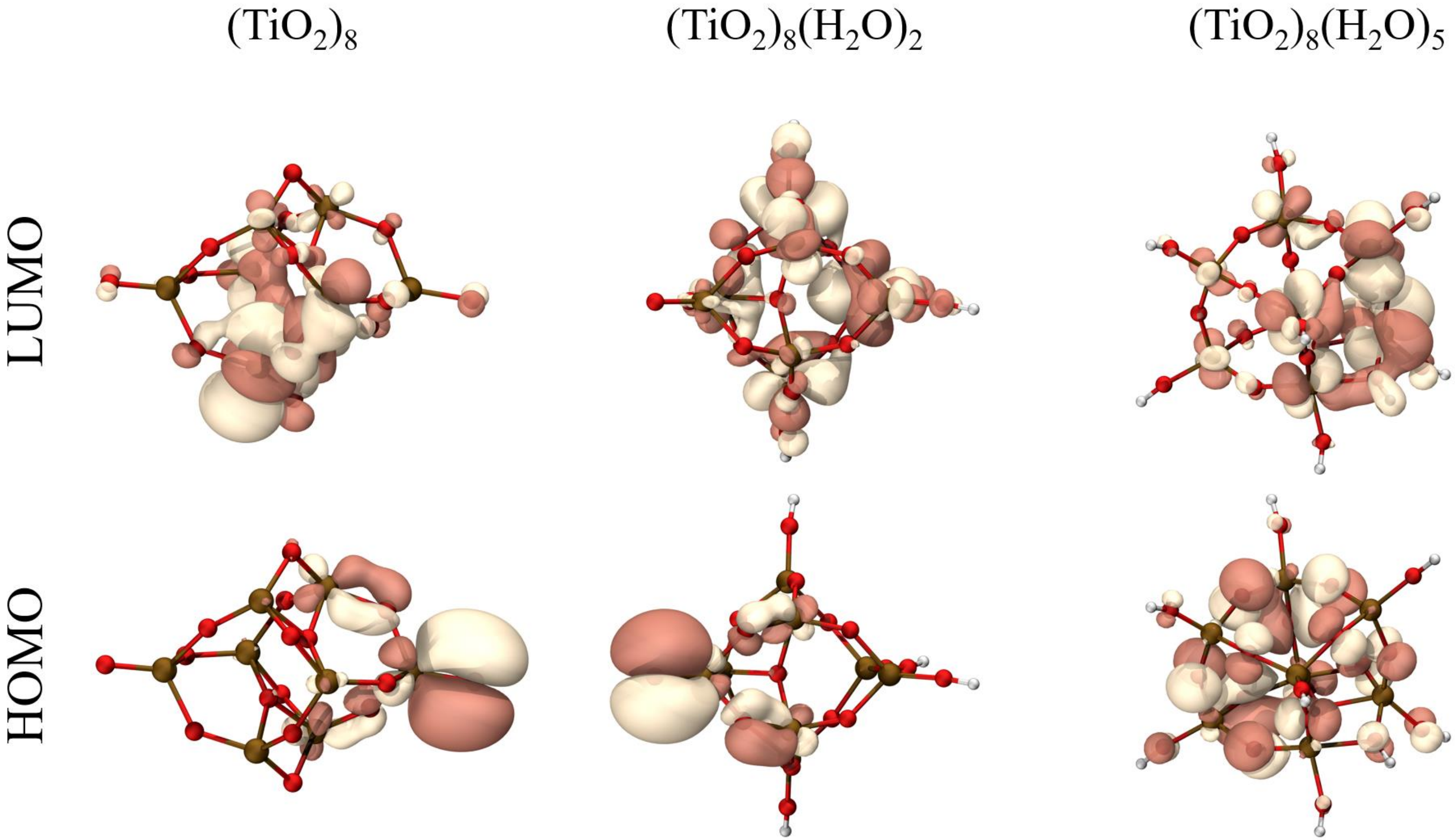

$(TiO_2)_8(H_2O)_5$

Bare case: $S_1 \rightarrow S_0$ transition is driven by the Ti-O-Ti angle bending mode

Hydrated clusters: **driven by** bending and stretching **modes**

Hydroxyl related **modes not coupled to the $S_1 \rightarrow S_0$ transition**

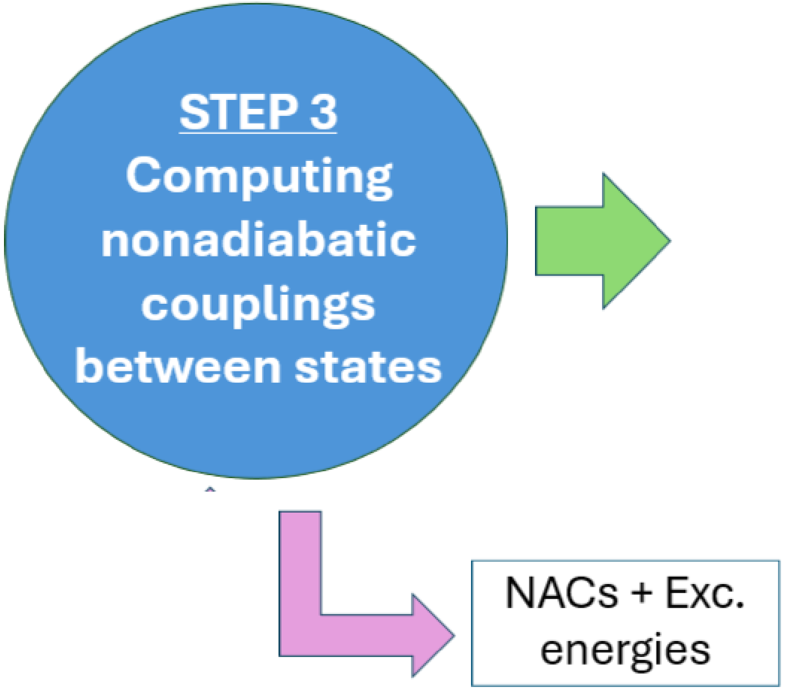
First project (step II)



Larger electronic **densities** located **around the Ti-O bonds.** Consistent with the spectra.

Excited state of **bare shows larger transition dipole moment**. Increasing **degree of hydration** -> excited state becomes **more symmetric**, leading to smaller TDM

First project (step III)



STEP 3

Computing nonadiabatic couplings between states

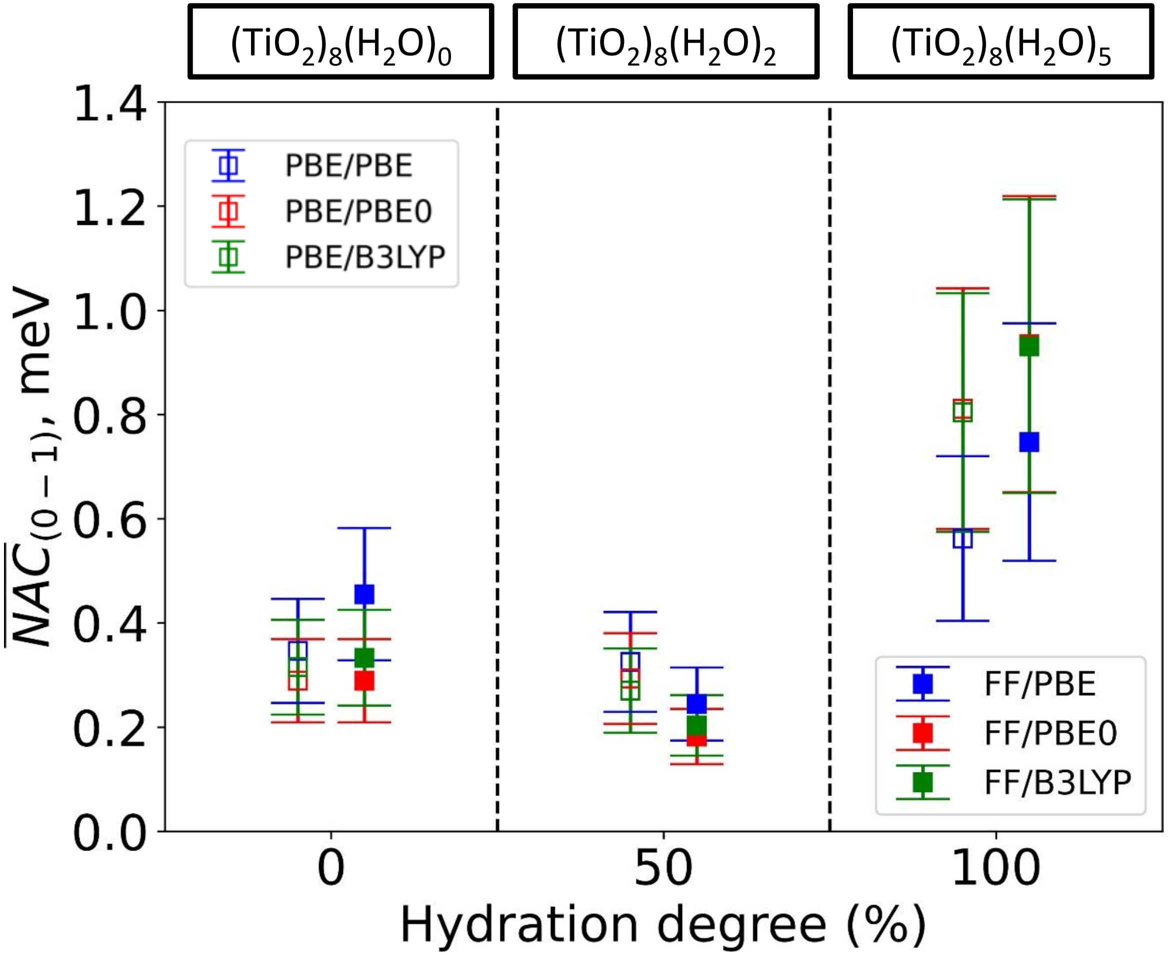
NACs + Exc. energies

Hammes-Schiffer-Tully (HST) approach for computing NACs:

$$d_{IJ}\left(t+\frac{dt}{2}\right) \approx \frac{\langle \Psi_I(t)|\Psi_J(t+\Delta t)\rangle - \langle \Psi_I(t+\Delta t)|\Psi_J(t)\rangle}{2dt}$$

where $\langle \Psi_\mathrm{I}(\mathrm{t})|\Psi_\mathrm{J}(\mathrm{t}+\Delta\mathrm{t})\rangle$ stands for the time overlaps computed in the previous step

First project (step III)

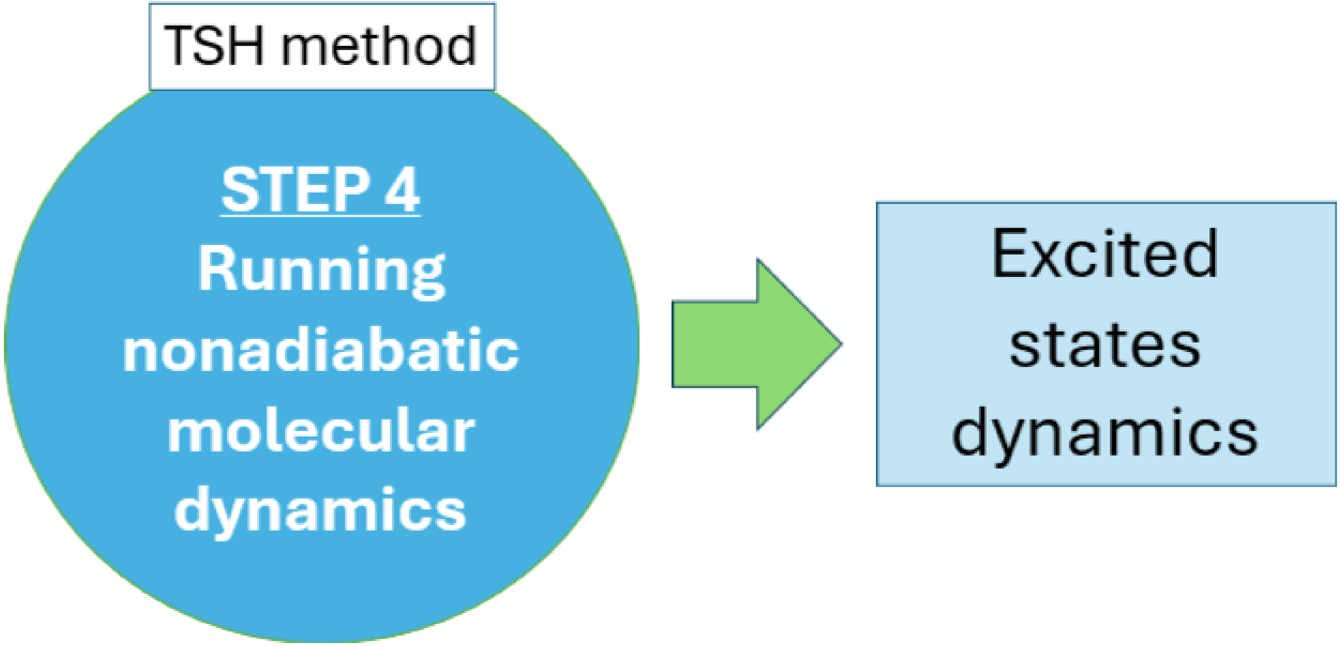


$(TiO_2)_8(H_2O)_2$ **presents lower average NACs than bare case** (states **more separated in energy**)

For largest degree: the states acquire similar spatial distributions

Fully hydroxylated system possess better electronic state mixing and thus **larger NACs**

First project (step IV)



TSH method

STEP 4

Running nonadiabatic molecular dynamics

Excited states dynamics

Pre-computed energies (E_I) and NACs (d_{IJ}) are used to construct **the vibronic Hamiltonian** at every timestep of the trajectory

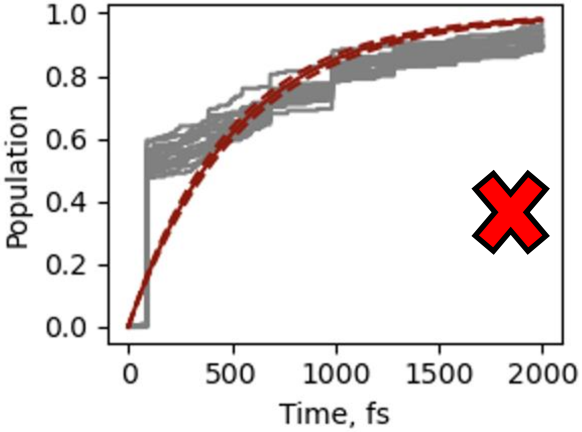
Trajectory surface hoping **(TSH) algorithms:** FSSH, mSDM, DISH, IDA

30 initial conditions x 500 realizations = **15000 trajectories per methodology**. NA-MD runs are **initialized in S_1** in all of them. Decay evolution fitted to exponential fitting functions

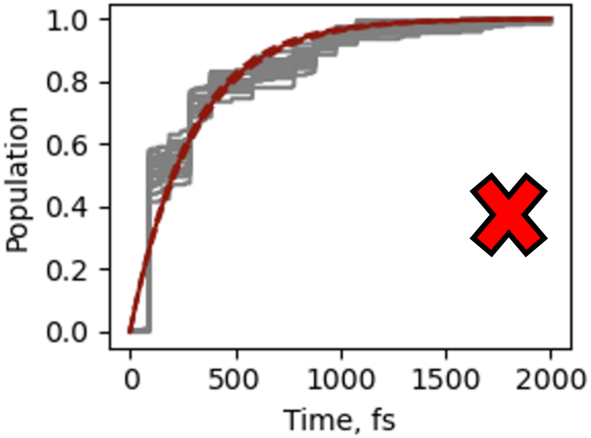
First project (step IV-problematics)

$(TiO_2)_4\ (H_2O)_4$ AIMD + B3LYP

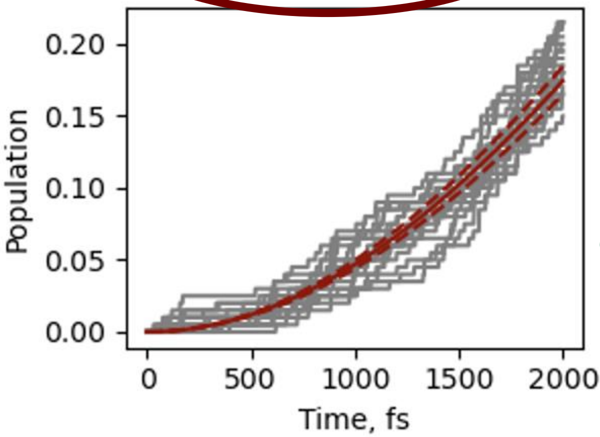
Files: 1500-1800



Files: 1500-1600



Files: 2000-3000



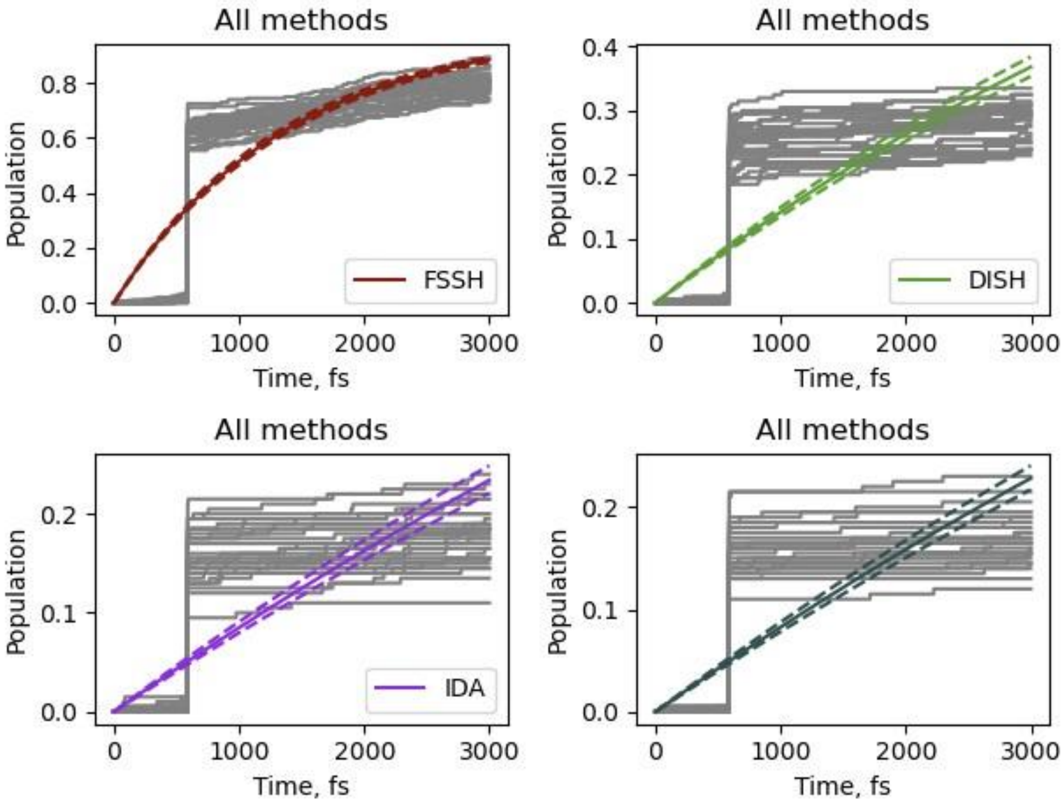
✓

We can play with which NACs and excitation energies we select and avoid the problematic step causing the sudden population change

Method: FSSH, ntraj: 200

First project (step IV-problematics)

$(TiO_2)_4 (H_2O)_4$ AIMD + B3LYP



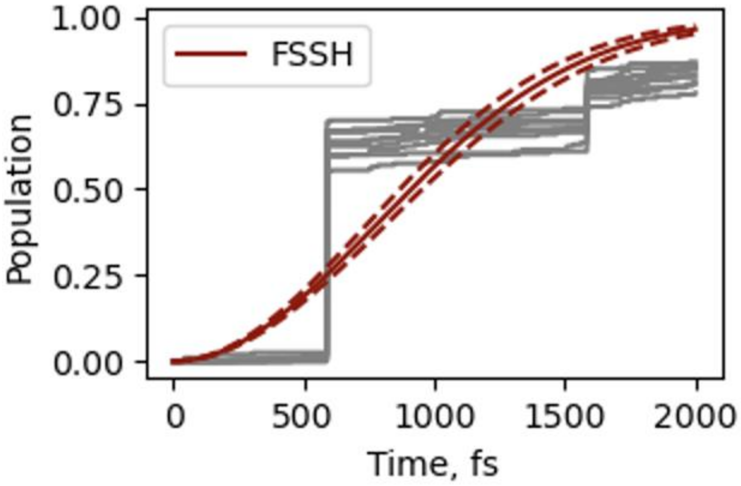
If we include 5 states in our dynamical basis… we have these sudden changes in Ground State population evolution

Method: FSSH, ntraj: 200, files: 1000-4000, steps: 3000

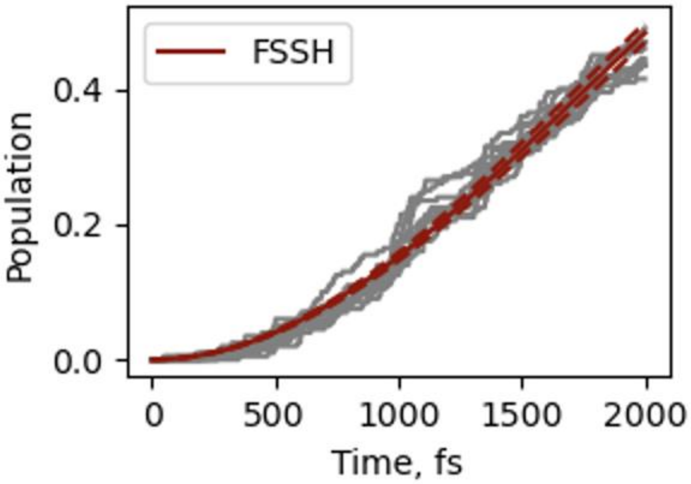
First project (step IV-problematics)

$(TiO_2)_4\ (H_2O)_4$ AIMD + B3LYP

By increasing the number of excited states in our dynamical basis -avoiding crosses with states that are not included in the basis- we can overcome our problem with the sudden changes in states pop. evolution



NSTATES = 5



NSTATES = 10

Method: FSSH, ntraj: 200, files: 1000-2000, nsteps: 2000

First project (step IV)

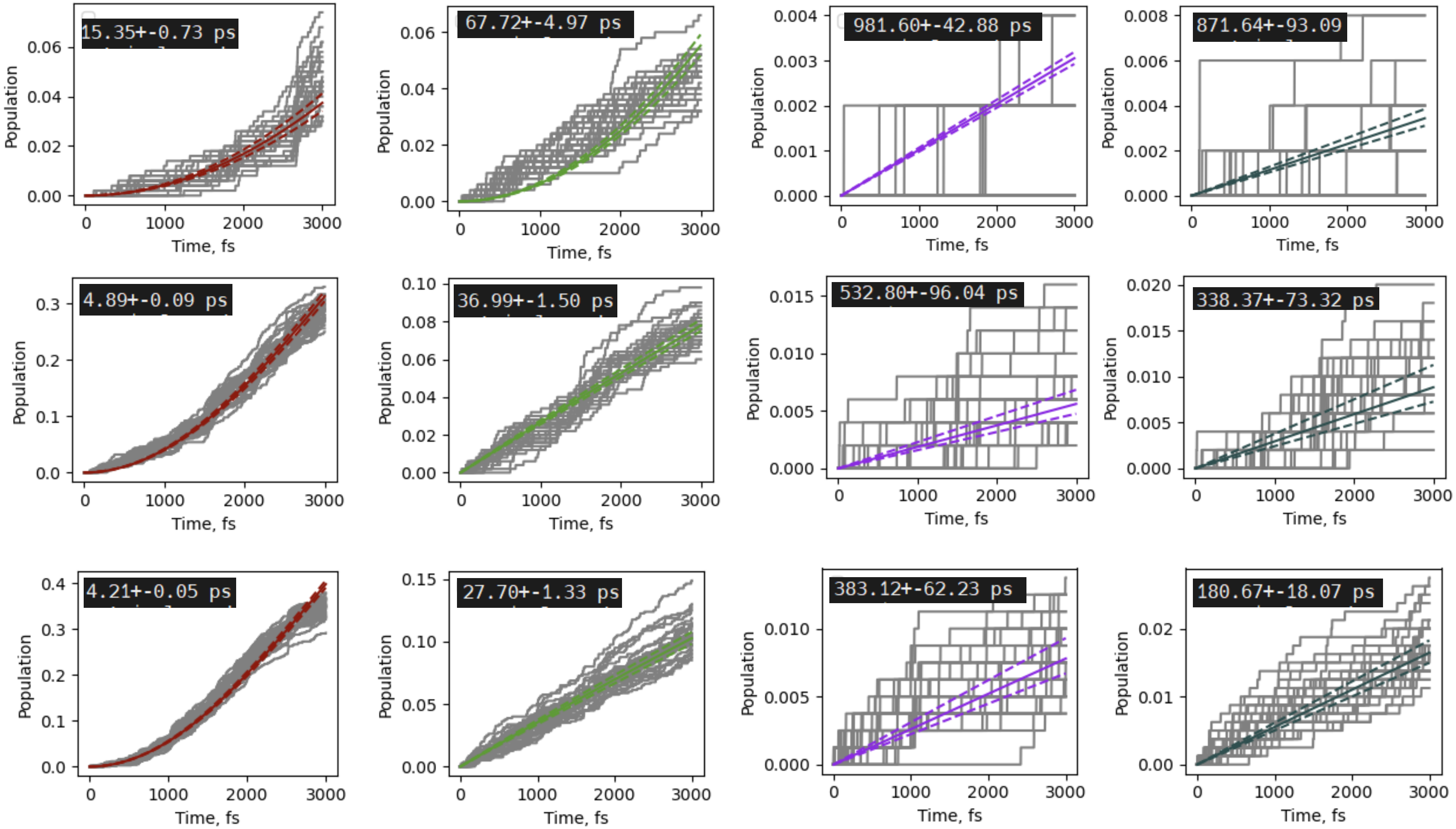
FSSH | DISH | MSDM | ID-A

AIMD + PBE

$(TiO_2)_4$

$(TiO_2)_4(H_2O)_2$

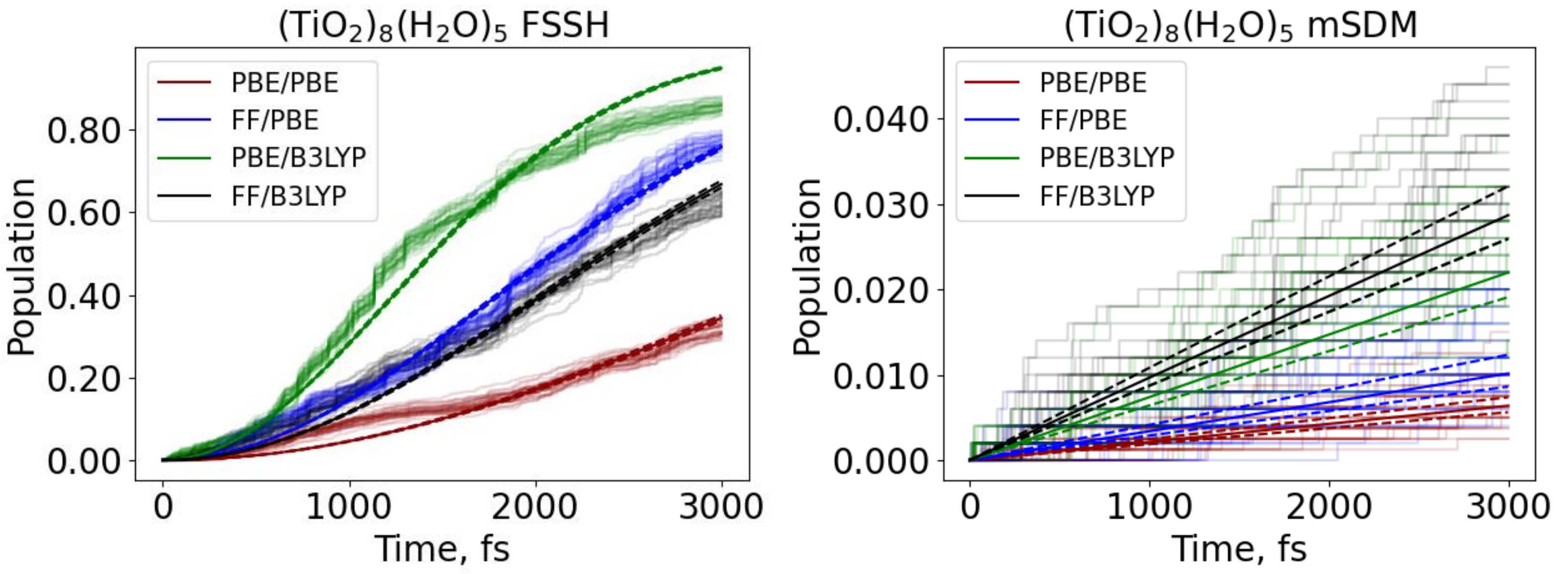
$(TiO_2)_4(H_2O)_4$



In all cases **FSSH yields shorter** e$^-$-h$^+$recombination **times**

Faster recombination evolution **with increasing** degree of **hydroxylation**

First project (step IV)



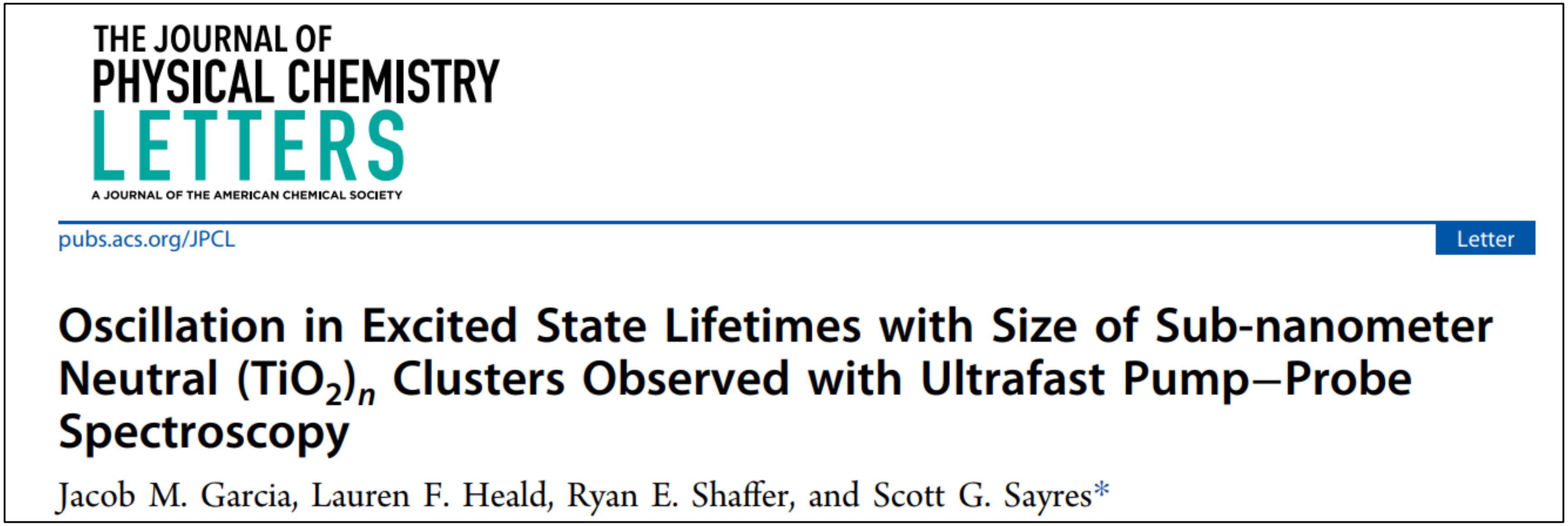
mSDM method involves a complex description **leading** to the elimination of coherences and thus **to larger decay**

Hybrid TD-DFT **functionals** give rise to **faster** S_1-S_0 **recombination**

Good agreement in final results between ffMD and AIMD!!

$(TiO_2)_8(H_2O)_2$ provides **longer times – more convenient** for photocatalysis

Second project: recombination or relaxation?



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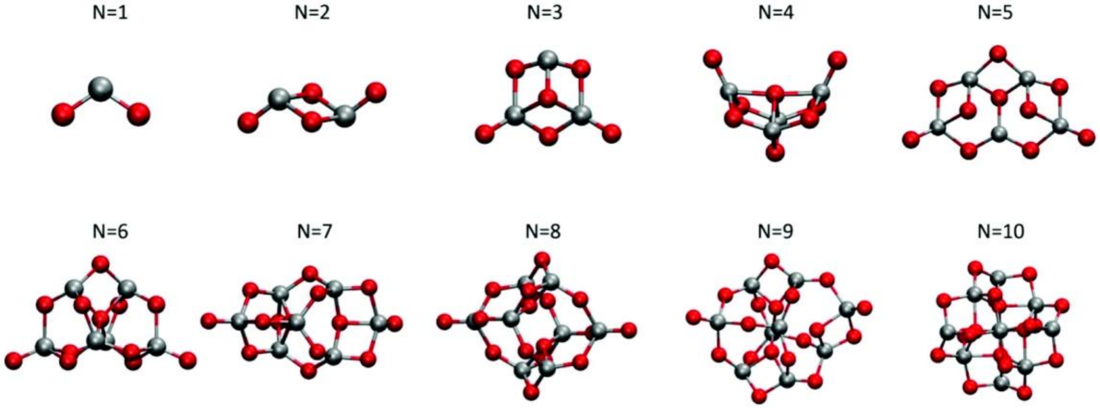
Letter

Oscillation in Excited State Lifetimes with Size of Sub-nanometer Neutral $(TiO_2)_n$ Clusters Observed with Ultrafast Pump–Probe Spectroscopy

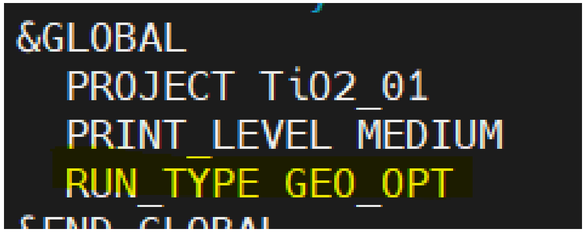
Jacob M. Garcia, Lauren F. Heald, Ryan E. Shaffer, and Scott G. Sayres*



sub-picosecond excited state lifetime (τ) is attributed to rapid internal conversion **returning to the ground state**.

Second project: Wigner sampling

RUN GEOMETRY OPTIMIZATION WITH CP2K
+ CALCULATION OF VIBRATIONAL FREQUENCIES



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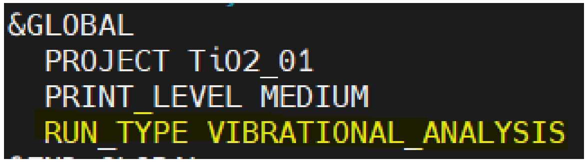

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TiO_2_01-VIBRATIONS-1.mol

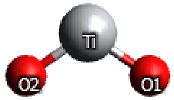
RUN wigner.py SCRIPT
(-n 100) (-t 300)

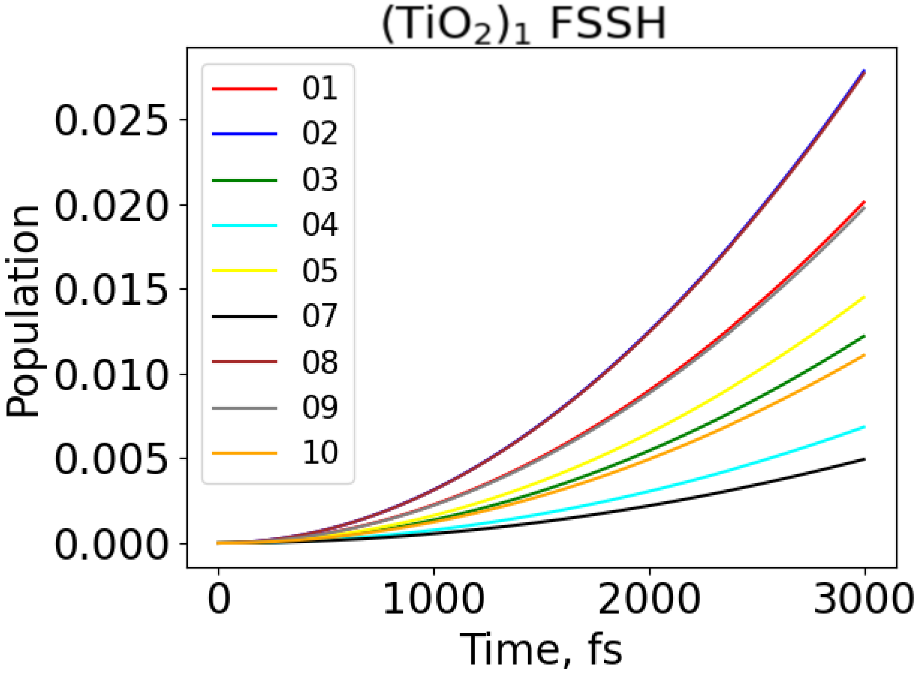
initconds file

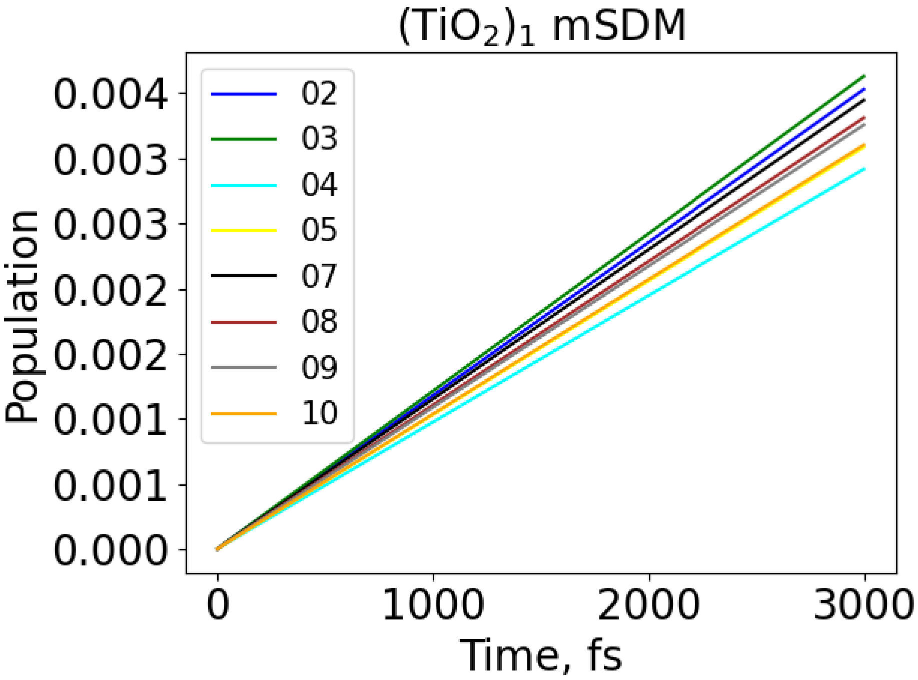
10 GEOMETRIES + VELOCITIES: RUN STEP1, STEP2 (CAM-B3LYP), STEP3, STEP4

COMPUTE AVERAGE VALUES

Second project




$(TiO_2)_1$ FSSH

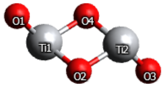

$(TiO_2)_1$ mSDM

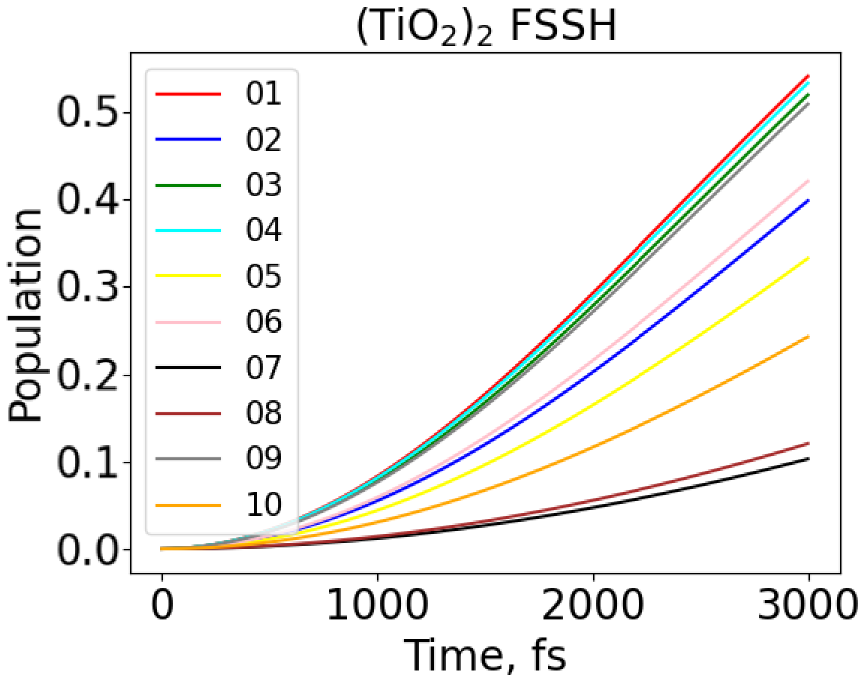
Average timescale: **26.34+-7.94 ps**

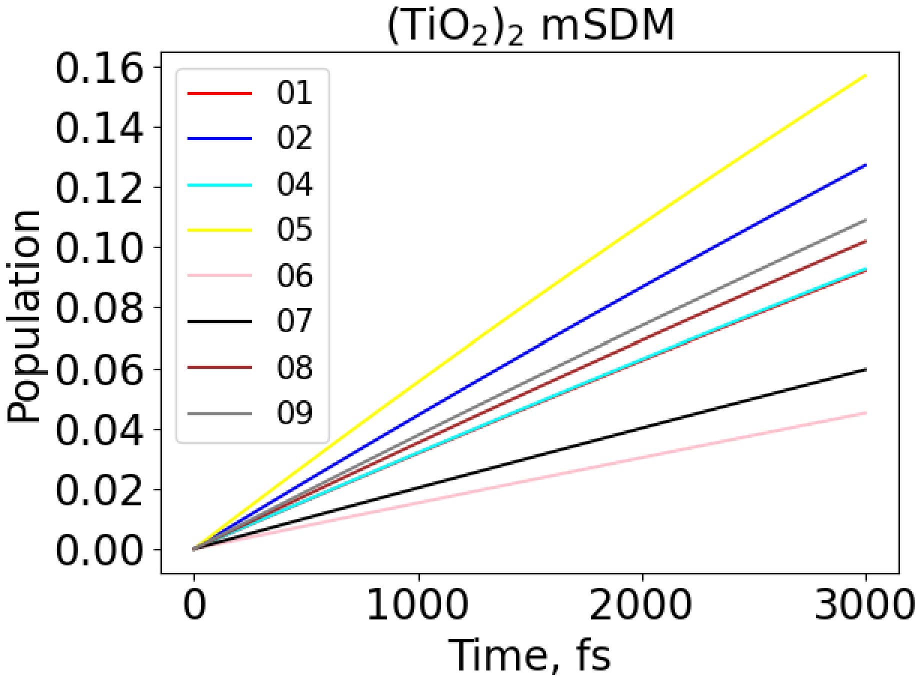
Average timescale: **915.95+-64.22 ps**

Several orders of magnitude bigger than the experimental times

Second project




(TiO$_2$)$_2$ FSSH

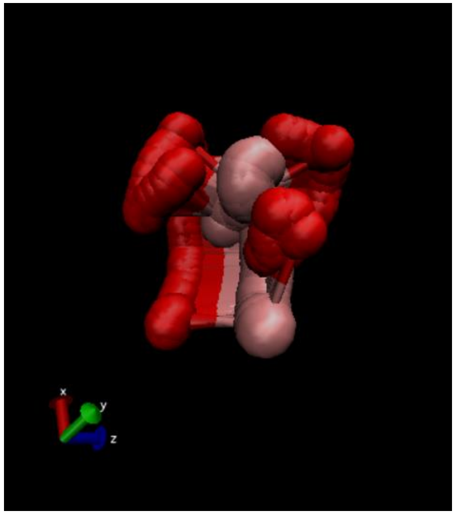

(TiO$_2$)$_2$ mSDM

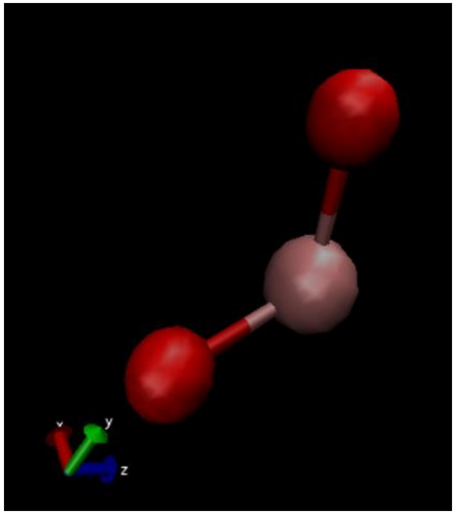
Average timescale: **5.00+-2.08 ps**

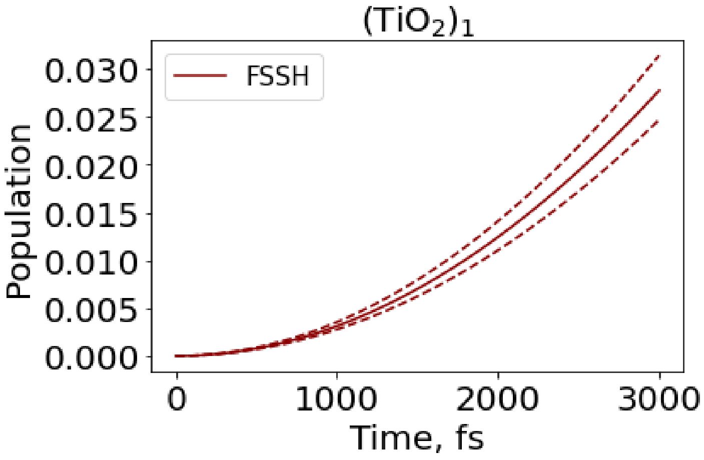
Average timescale: **33.67+-14.65 ps**

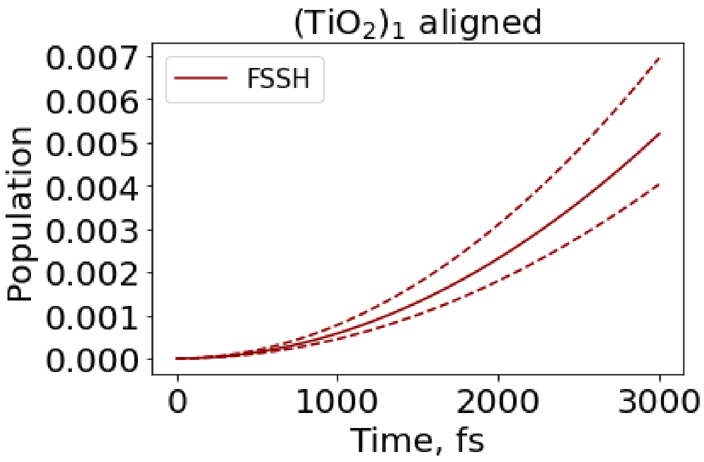
Several orders of magnitude bigger than the experimental times

Second project: trajectory aligment





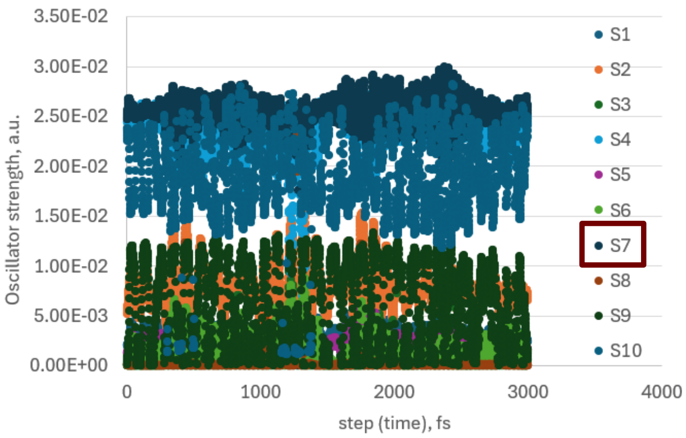


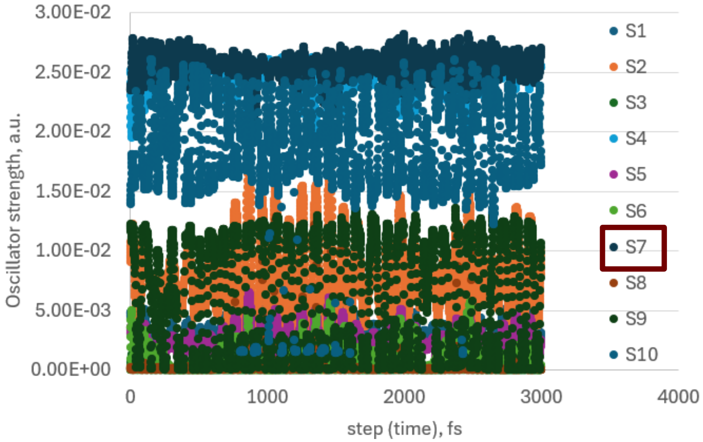


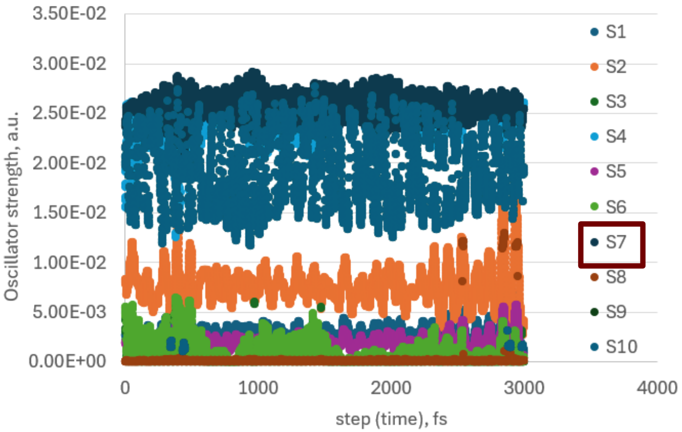
Average timescale: **17.89+-1.09 ps**

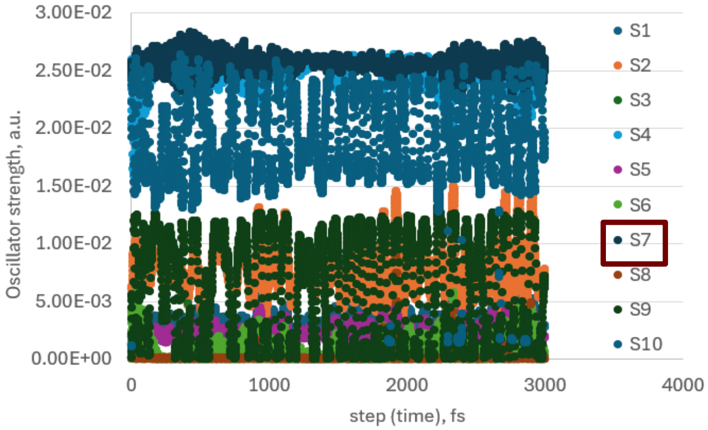
Average timescale: **41.56+-5.64 ps**

Second project: Oscillator Strength TiO_2



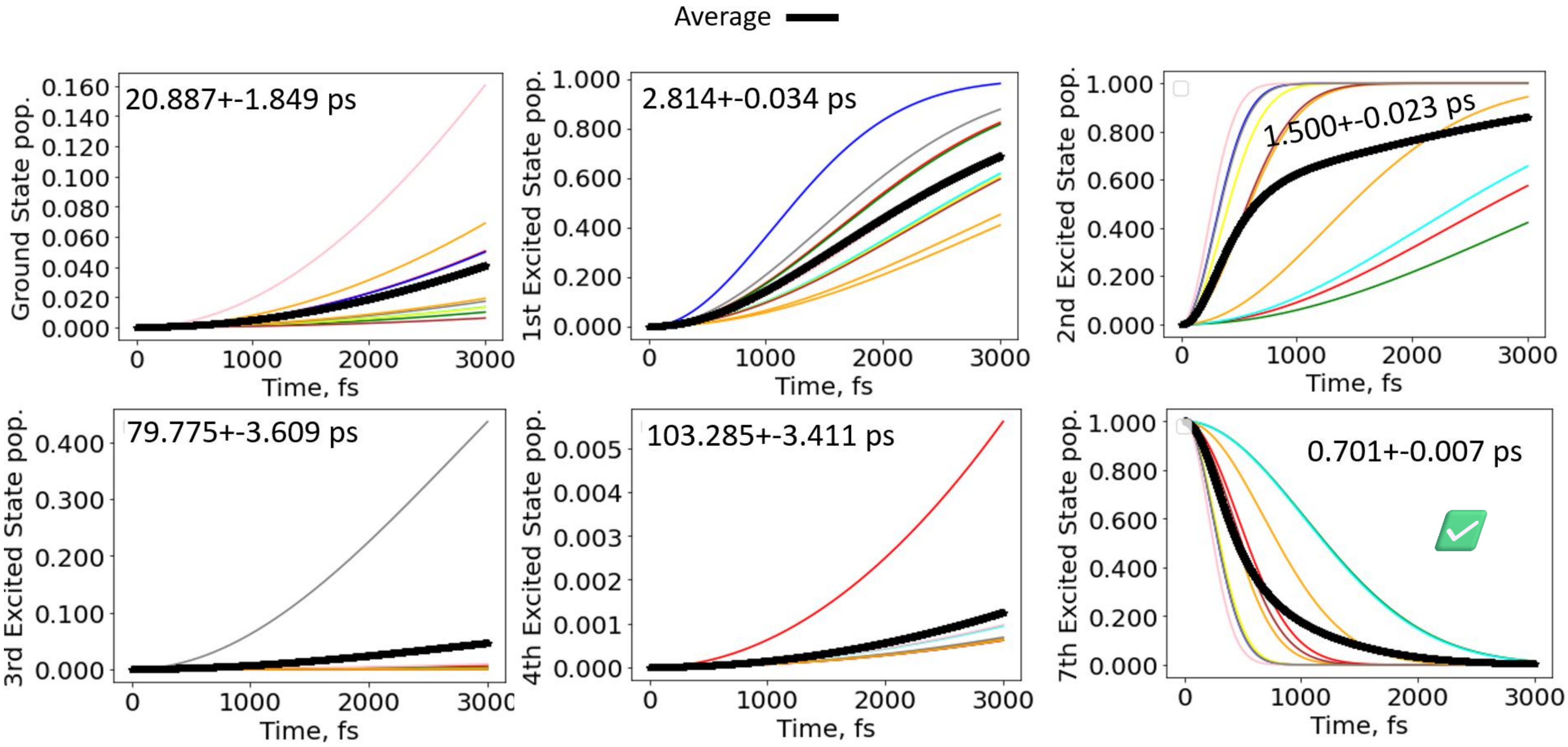






Second project: TiO$_2$

TiO$_2$ FSSH (istate=7)



Conclusions

- ✓ Libra (interchanged with CP2K) provides a complete workflow to analyse excited state dynamics in titania systems.

- ✓ Influence of water in general reduce recombination times, as NACs increase. Methodology assessment: ffMD is efficient counterpart to AIMD. Hybrid functionals give rise to faster S_1-S_0 recombination.

- ✓ Small anhydrous calster undergo fast relaxation among optical levels that has been overlooked in experimental research.

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$2H_2O \rightarrow 2H_2 + O_2$
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