Mechanisms and Methodologies for Modelling Excited-State Dynamics in Bare and Hydrated TiO_2 Nanoclusters

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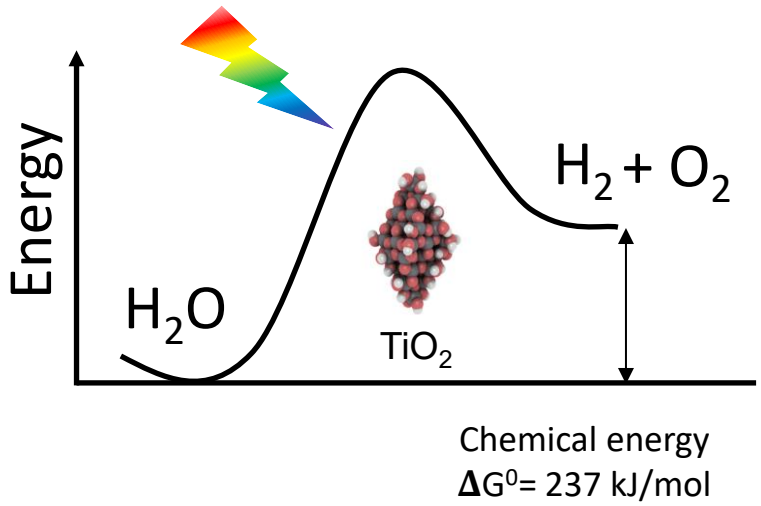
Role of TiO_2 in photocatalysis

Titania (TiO_2) is a widely used metal oxide in both industrial and environmental applications. **Water splitting**.

H_2 : Clean energy source but against thermodynamics.



Need of external energy. **Photocatalytic water splitting**. **Anatase titania** as a potential solution.

Bandgap is too large (3.2 eV). Absorbs only a **small fraction** of solar spectrum. High **recombination rate** of electron-hole pairs.

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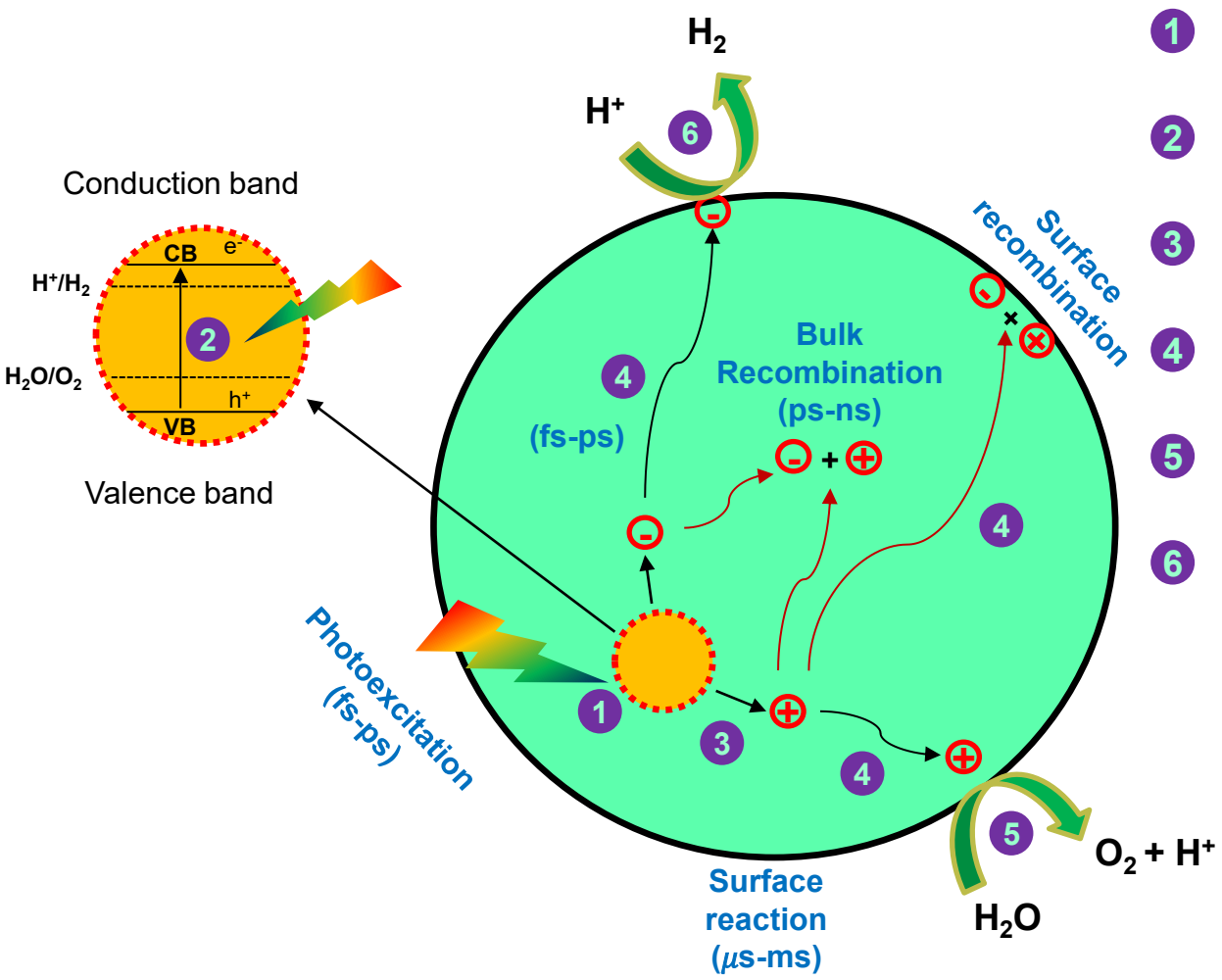
Key steps in photocatalytic water splitting



1. **Light irradiation/harvesting**
2. **Electron-hole generation**
3. **Electron-hole separation**
4. **Electron-hole transportation to the surface**
5. **Oxidation reaction**
6. **Reduction reaction and H_2 generation**

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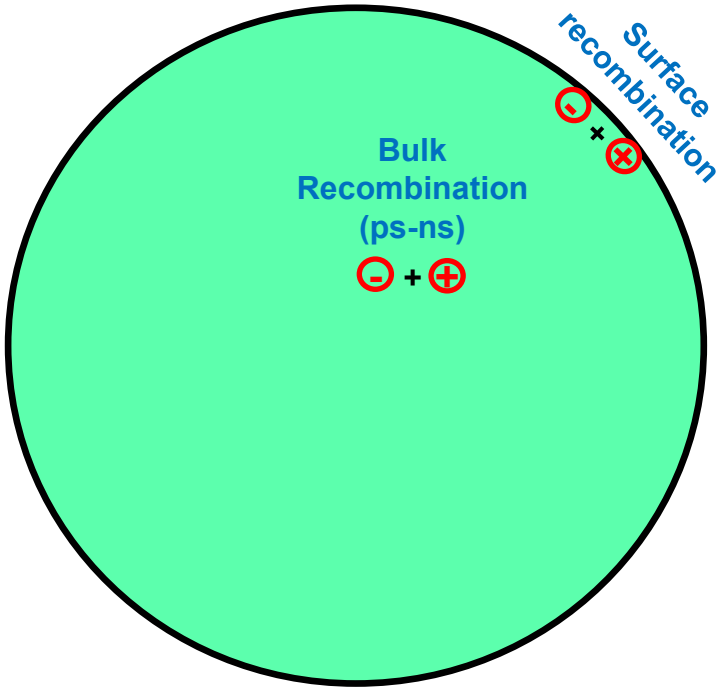
Modelling excited state dynamics



TiO_2 is a stable, abundant photocatalyst—but limited by **fast electron–hole recombination**

Can we tune or extend such recombination times?

Studying excited state: **Nonadiabatic molecular dynamics** (nanostructuring, hydration,…)

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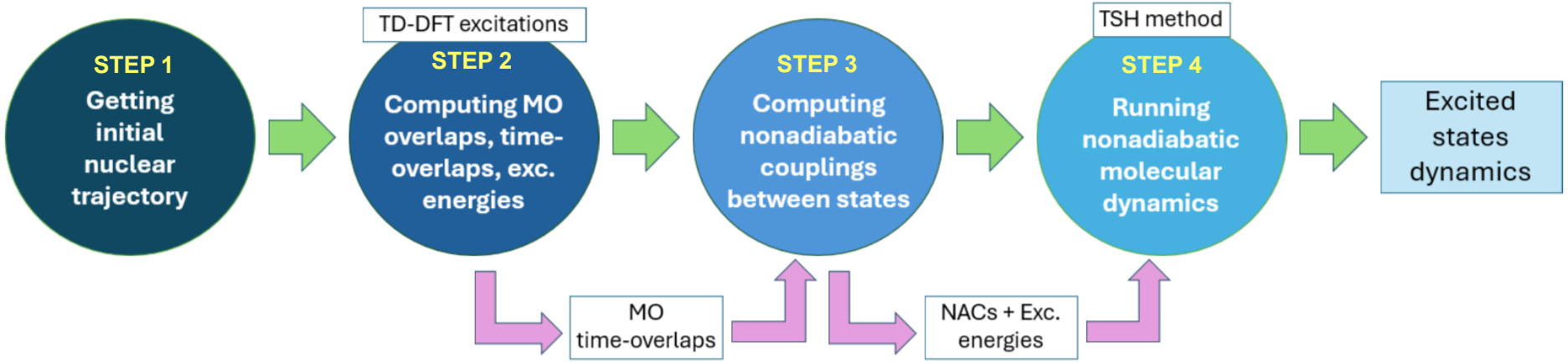
Nonadiabatic Molecular Dynamics workflow



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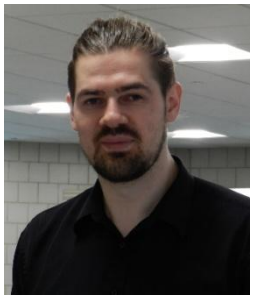

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- **CP2K**: step 1, step 2 (excitations)
- **Libra**: step 2 (overlaps), step 3, step 4

A. V. Akimov, J. Comput. Chem. ***2016****, 37, 1626-1649*

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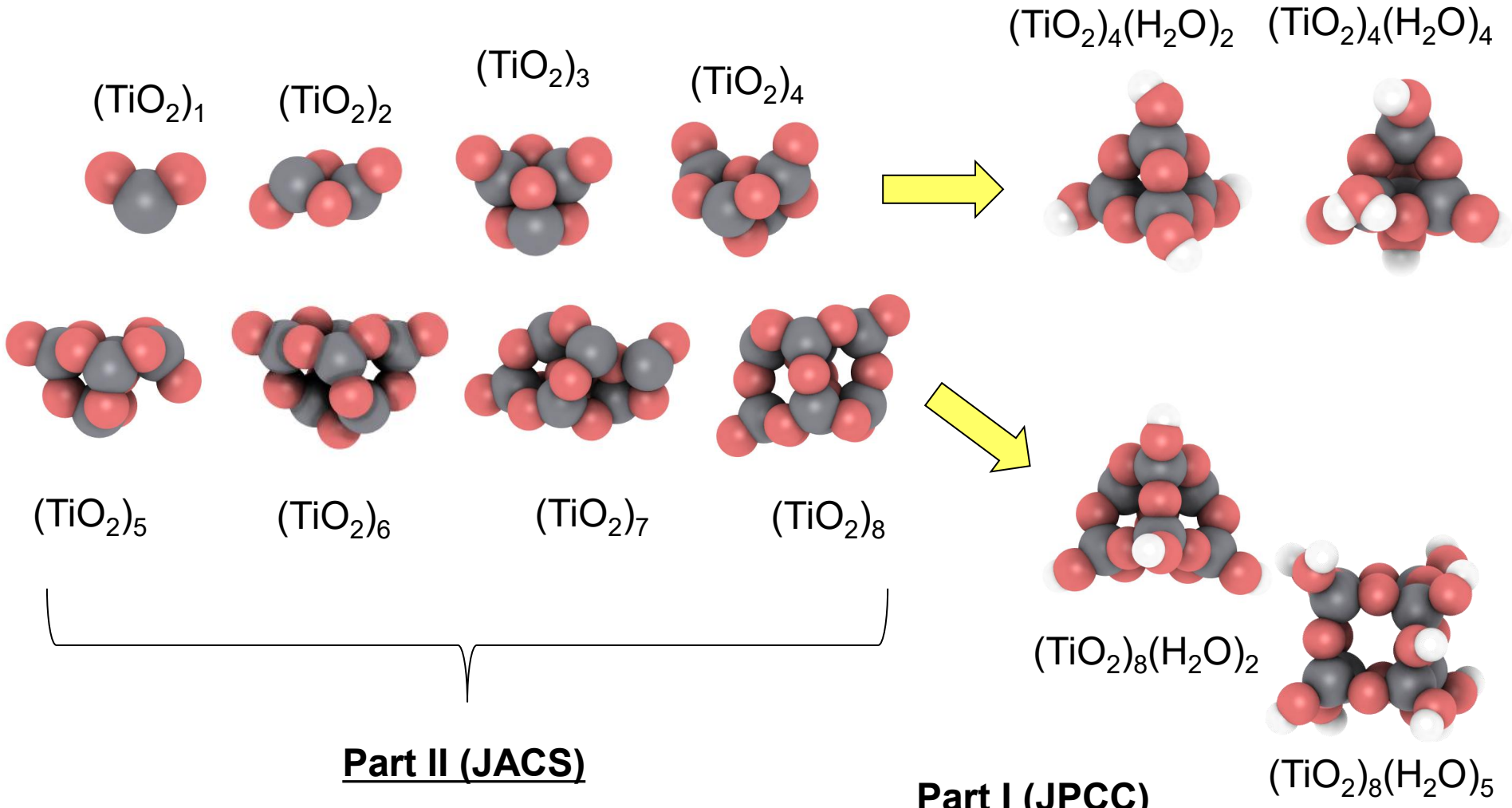
Model Systems: TiO_2 Nanoclusters

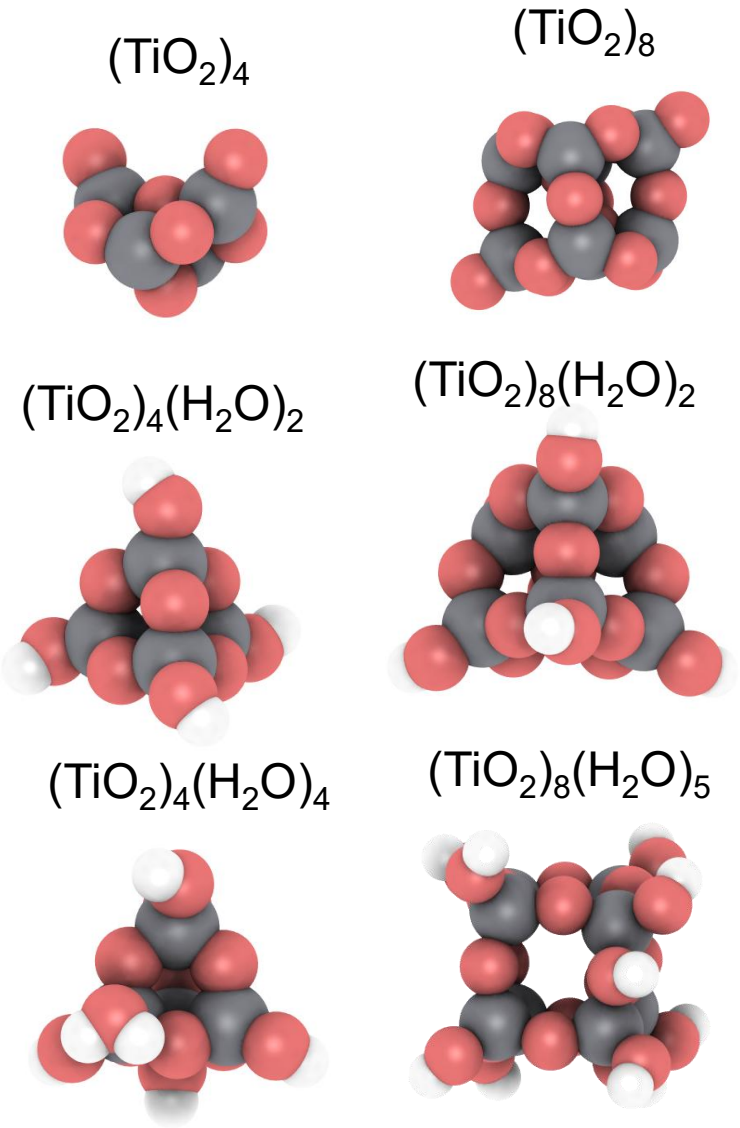


Part I – Hydration and Methodology Assessment

Dependence of excited state dynamics on **the hydration degree**

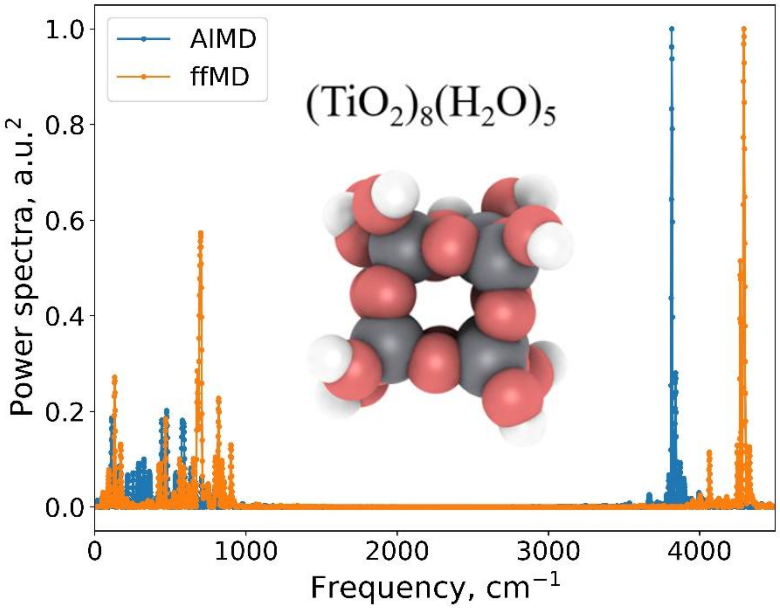
$\mathbf{S_1 \rightarrow S_0}$ (electron-hole recombination)

Benchmark common TD-DFT and NA-MD **methodologies**

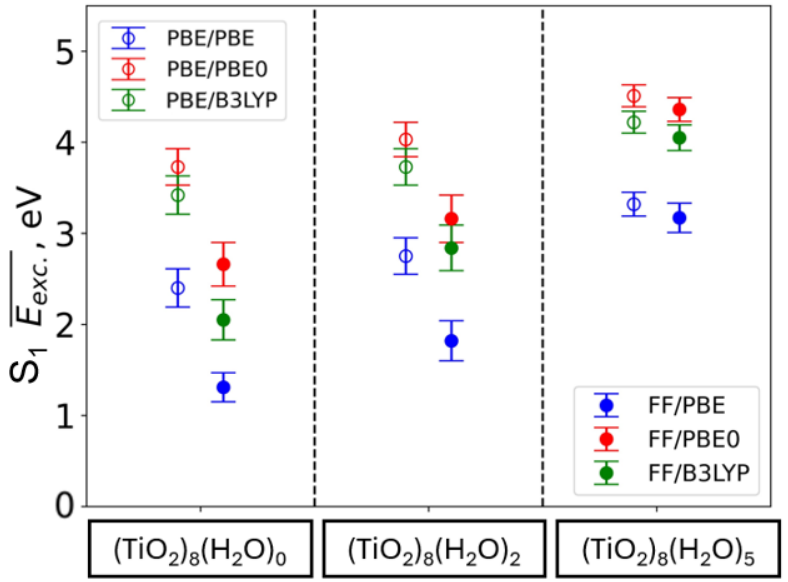


Part I - Vibrational and electronic structure

Classical Dynamics (NanoTiO & FFTiOH)
***Ab initio* Molecular Dynamics (PBE)**
4 ps run (1 ps equilibration + 3 ps production):**3000 structures**



S_0 to S_1 state transition
PBE, PBE0 and B3LYP functionals



100 to 200 cm^{-1} -> Ti-O-Ti **angle bending**

500-1000 cm^{-1} -> Ti-O **stretching**

Hydroxyl **stretching mode around 4000** cm^{-1}

Hydration increases excitation **S_1 energies**
Hybrid functionals **mitigate underestimation**
$S_1 \rightarrow S_0$ transition **driven by** Ti-O **modes**

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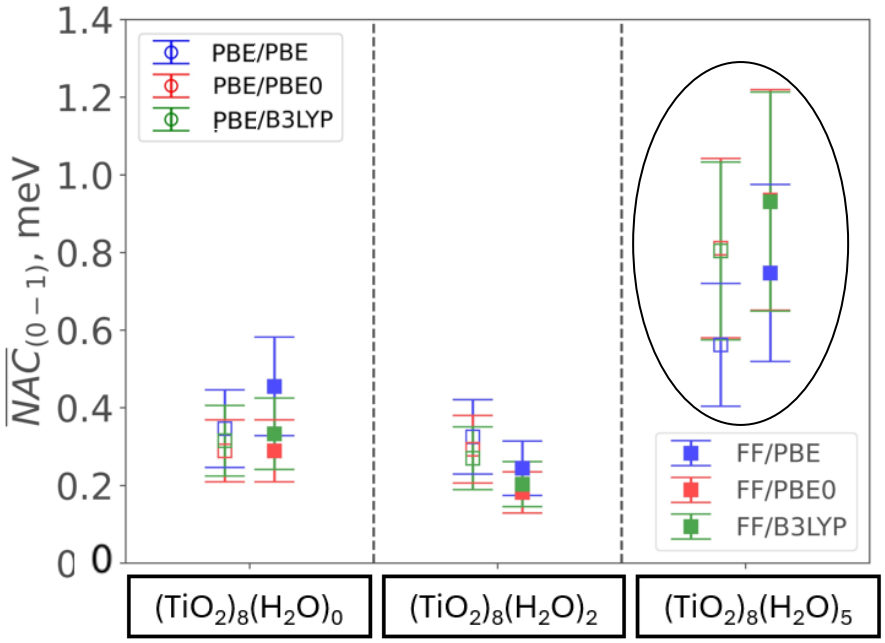
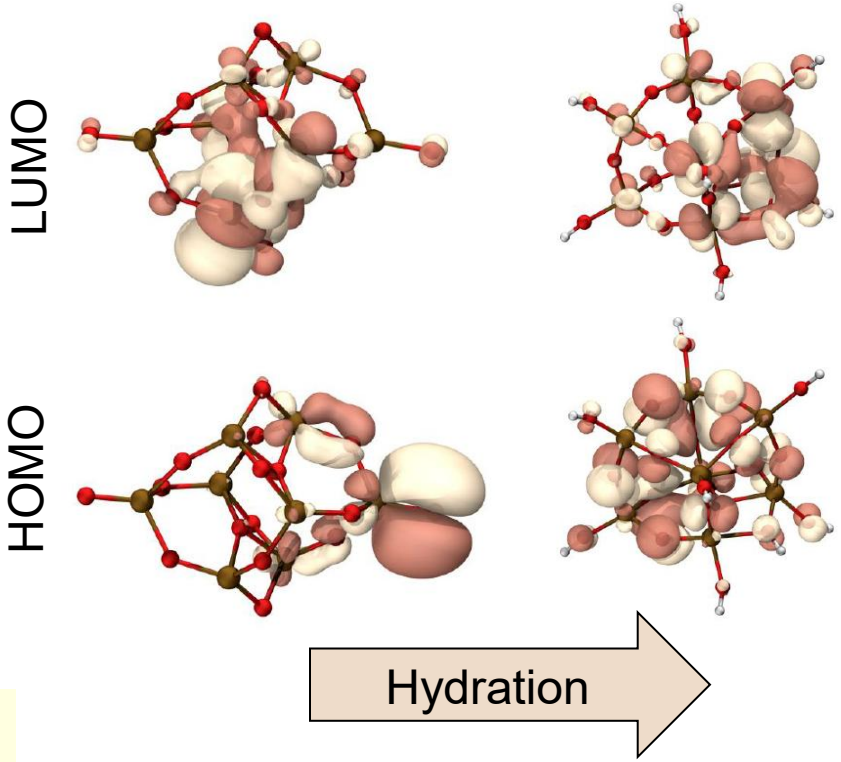
J. Phys. Chem. C ***2025****, 129 (3), 1806*

Part I - Nonadiabatic Couplings

Hammes-Schiffer-Tully (HST) approach:

$$d_{i,j}\left(t+\frac{\Delta t}{2}\right) \approx \frac{\langle \Psi_i(t)|\Psi_j(t+\Delta t)\rangle - \langle \Psi_i(t+\Delta t)|\Psi_j(t)\rangle}{2\Delta t}$$





Competition between energy difference and **isotropy**

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Part I - Nonadiabatic molecular dynamics

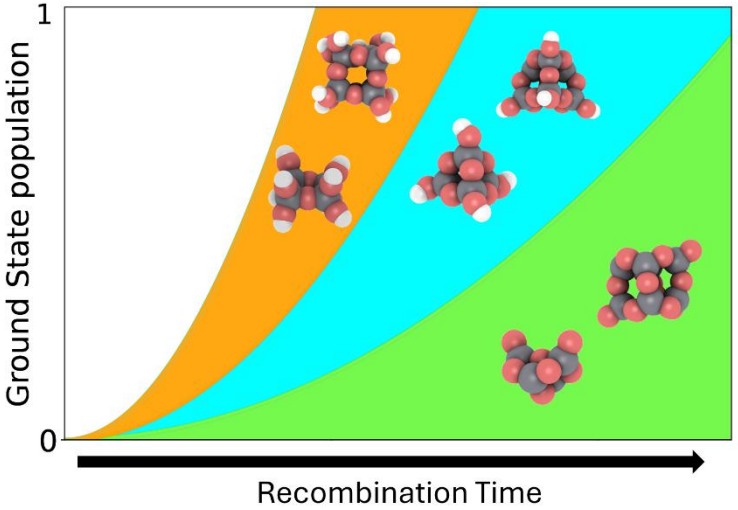
$$H_{ij}^{vib}(\mathbf{R}(t)) = E_i(\mathbf{R}(t))\delta_{ij} - i\hbar d_{ij}(\mathbf{R}(t))$$

TSH methods:

FSSH, DISH, ID-A, **mSDM**

NA-MD **initialized in S_1**

15000 trajectories per methodology



$$f(t) = 1 - \exp\left(-\frac{t}{\tau}\right)^{\beta}$$

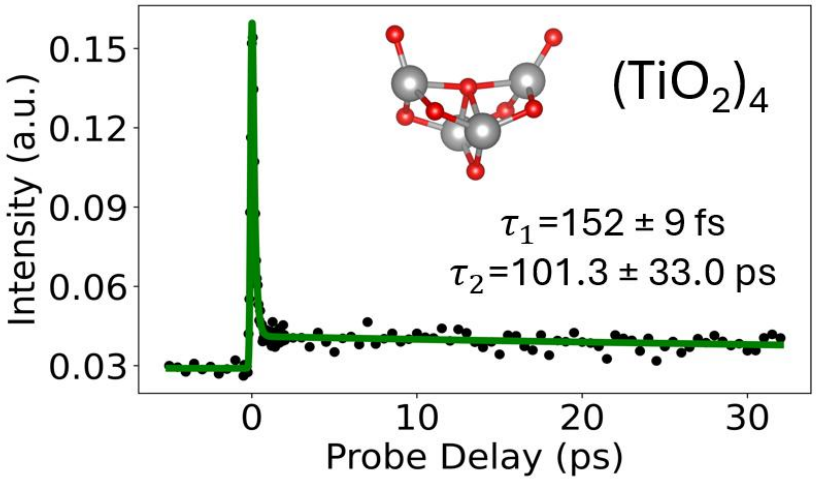
Decay evolution fitted to exponential fitting functions

- ✓ Hydration increases electron-hole recombination rates.
- ✓ Hybrid functionals and decoherence-corrected methods produce accurate predictions of excited-state dynamics. FFMD vs AIMD agreement.

Part II – Relaxation vs recombination

Investigating ultrafast relaxation and recombination in atomically precise **$(TiO_2)_n$** (n = 1–8) **nanoclusters**.

Experimentally recorded transient absorption signals



Pump: 266 nm, **4.66 eV**; Probe: 800 nm
Two lifetimes: **τ_1: ultrafast relaxation to S_1;**
τ_2: slower recombination to S_0.

Relaxation: $E(t) = \sum_{i=0}^{N} p_{i,SH}(t) E_i(t)$

Recombination well-captured by population of S_0

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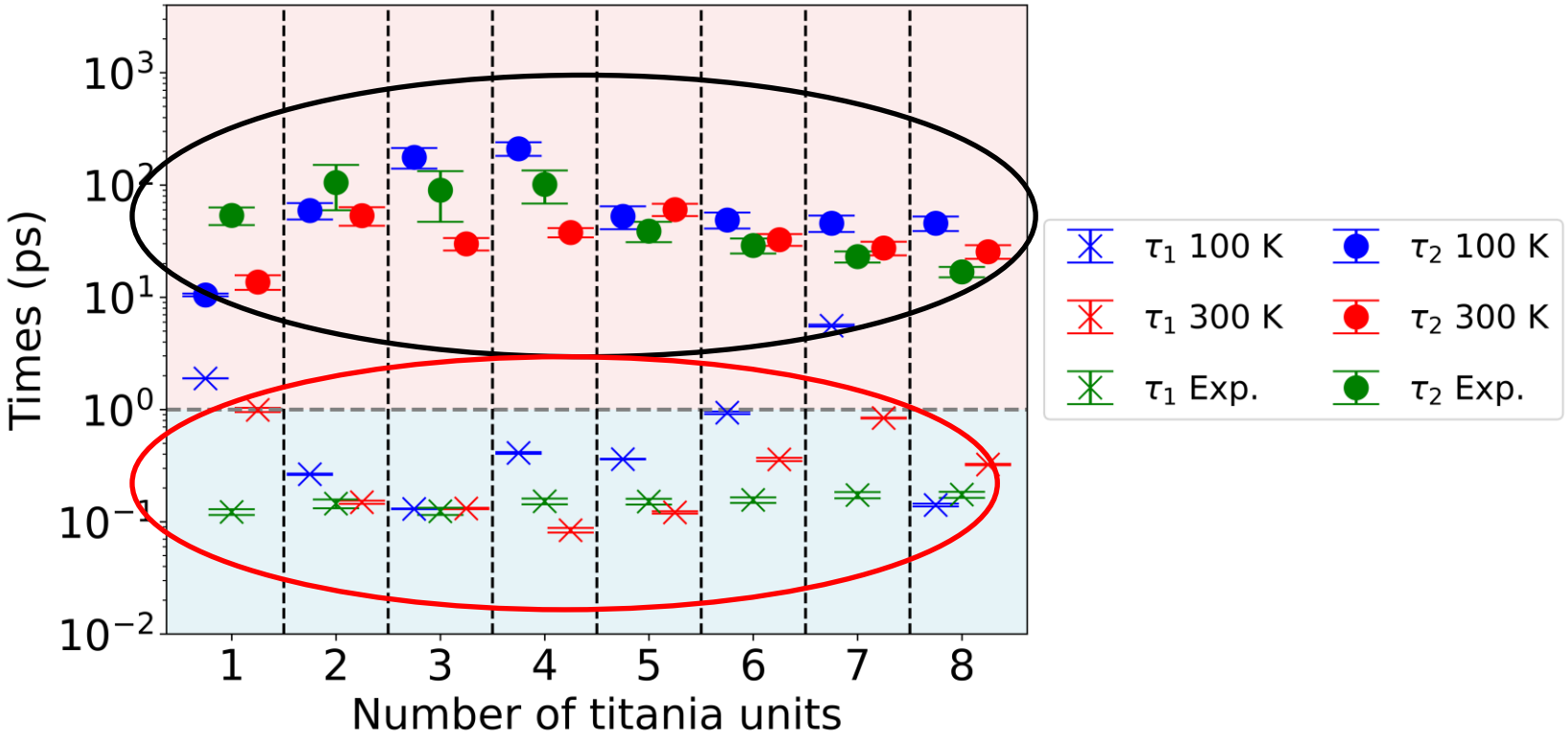
J. Am. Chem. Soc. ***2025****, 147, 40900–40909*

Part II – Agreement and trends



Recombination to S_0 (τ_2) depends **non-monotonically** on the cluster size:
-Slows down when $n \leq 4$
-Accelerates in larger systems

Slower relaxation to S_1 (τ_1) in **larger clusters**

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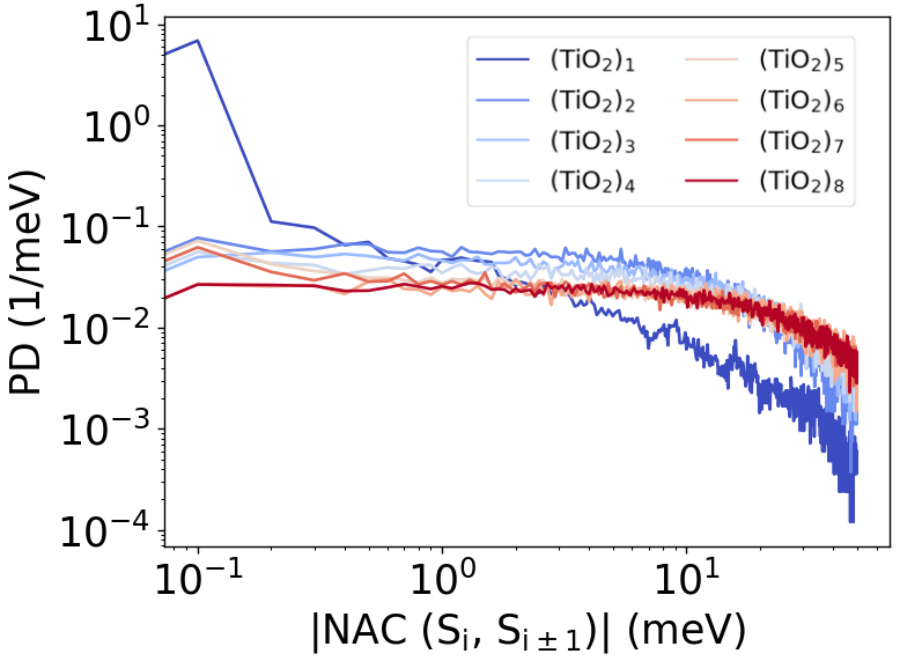
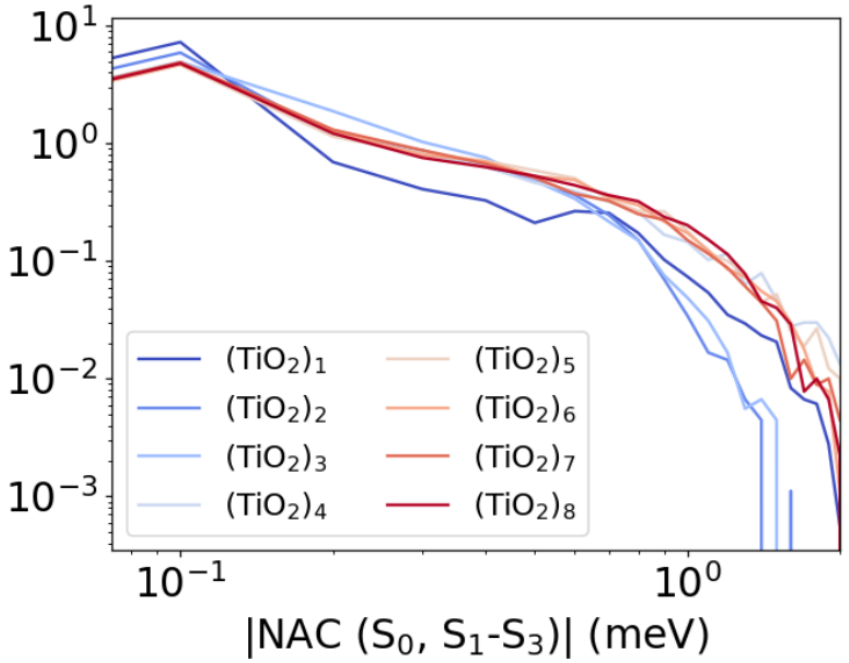
Part II – Mechanistic explanation





Larger NACs between adjacent states are more probable for larger clusters: **population spreading** among higher-energy states leading to **larger τ_1**

Larger 0-1:3 NACs also accelerate recombination in larger systems.

Larger clusters → **greater atomic fluctuations** (higher RMSD).

J. Am. Chem. Soc. ***2025****, 147, 40900–40909*

Conclusions

- ✓ Influence of water increases excitation energies and generally NACs. Indirect influence: Hydroxyl related modes not coupled to $S_0 \rightarrow S_1$ transition. **Hydration increases electron-hole recombination rates.**

- ✓ Hybrid functionals and decoherence-corrected methods produce accurate predictions of excited-state dynamics. **FFMD vs AIMD agreement**.

- ✓ **Two universal pathways** identified in $(TiO_2)_n$ (n = 1–8): Ultrafast relaxation ($\tau_1 \rightarrow S_1$) and slower recombination ($\tau_2 \rightarrow S_0$).

- ✓ Atomic flexibility and multiconfigurational mixing grow with size → boosts NACs couplings and alters lifetimes. **Mechanistic explanation** for observerd trends.

- ✓ Strong experiment–theory agreement → validates **Libra + CP2K NA-MD workflow** as a predictive tool to analyse excited state dynamics in titania systems.

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Acknowledgments

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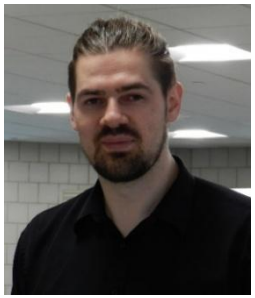

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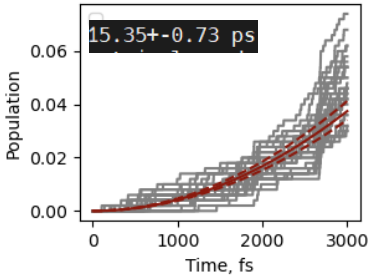
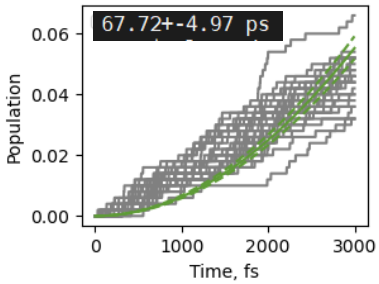
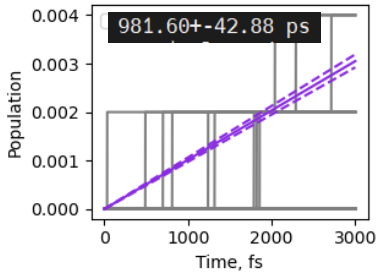
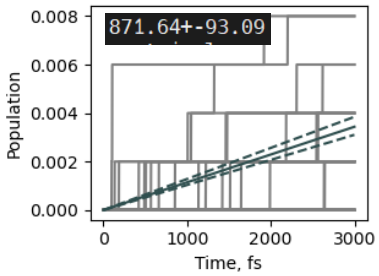
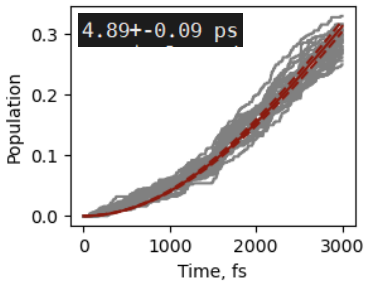
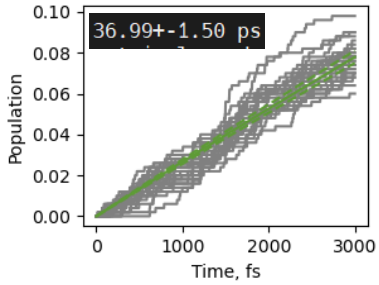
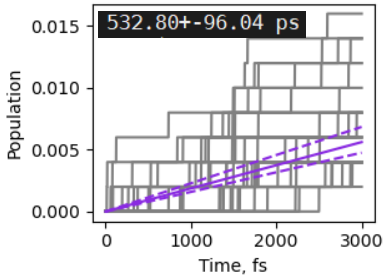
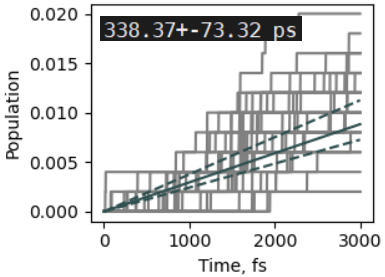
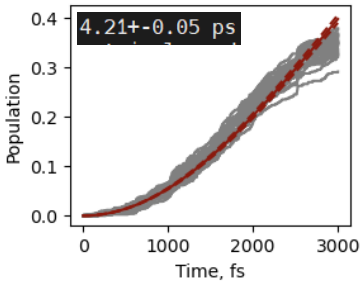
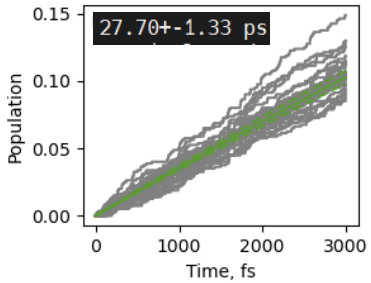
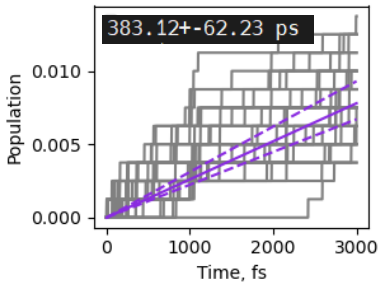
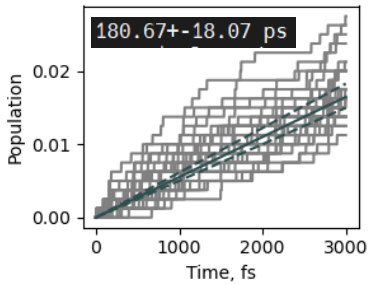
EXTRA

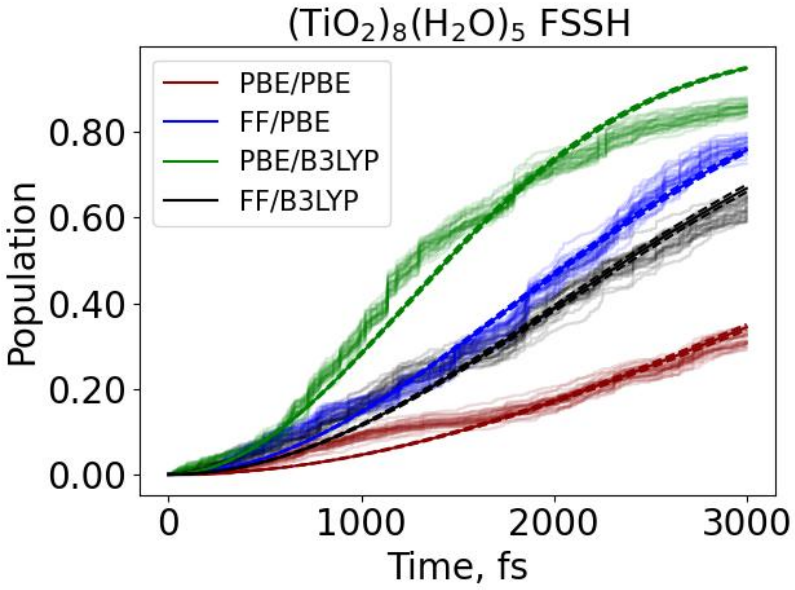
AIMD + PBE

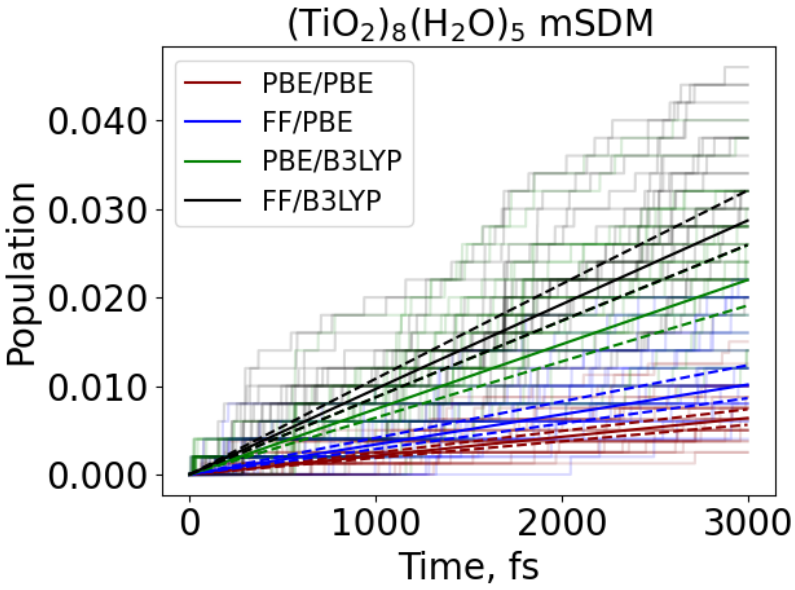
	FSSH	DISH	MSDM	ID-A
$(TiO_2)_4$				
$(TiO_2)_4(H_2O)_2$				
$(TiO_2)_4(H_2O)_4$				

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

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

EXTRA





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

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Structure–Dynamics Connection

Larger clusters → **greater atomic fluctuations** (higher RMSD).

Table 1. Toward Analysis of NACs in $(TiO_2)_n$ Nanoclusters[a]

	N		state index		RMSD (O), Å		RMSD (Ti), Å	
	T (K)		T (K)		T (K)		T (K)	
$(TiO_2)_n$	100	300	100	300	100	300	100	300
$(TiO_2)_1$	2	2	10	10	0.024	0.024	0.011	0.011
$(TiO_2)_2$	9	11	6	7	0.062	0.071	0.024	0.030
$(TiO_2)_3$	17	15	6	7	0.057	0.119	0.039	0.071
$(TiO_2)_4$	13	13	11	11	0.052	0.084	0.031	0.059
$(TiO_2)_5$	17	14	8	10	0.062	0.125	0.037	0.074
$(TiO_2)_6$	25	24	9	9	0.075	0.141	0.042	0.102
$(TiO_2)_7$	19	26	3	5	0.079	0.150	0.055	0.108
$(TiO_2)_8$	22	20	4	4	0.082	0.149	0.057	0.083

The first four columns quantify the degree of configurational mixing: number of determinants contributing to TD-DFT wf.

Other columns show the RMSD of oxygen and titanium atoms at 100 and 300 K.

Larger atomic fluctuations cause stronger perturbations of the electronic density resulting in larger NACs.