

Directly Track Carrier Transport in Interfaces and Chemical Reactions by First principle

Fan Zheng, Lin-wang Wang

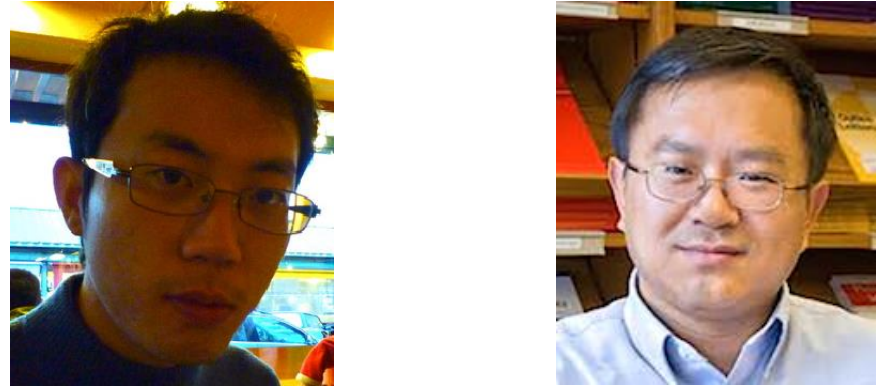
Abstract:

The lack of first-principle's methods to directly reveal the processes of carrier transfers makes it challenging to understand the fundamentals of electrochemical systems. By using the recently developed non-adiabatic molecular dynamics (NA-MD) and real-time time-dependent density functional theory (rt-TDDFT), we illustrate the full profiles of hot carrier cooling in interfacial systems and explore the significance of non-adiabaticity (NA) in reactions. The Schottky barriers and device design strategy could strongly suppress the back-transfer and enhance charge separation. By using one step of CO₂ reaction as an example, we find that conventional ground-state methods calculated reaction barriers could be underestimated. Moreover, we are developing new methodologies to expand current NA-MD and TDDFT capability. By including many-body effects, exciton dynamics in low-dimensional materials can be studied by first-principle. Molecular damage under solvent is also explored with wavefunction collapsing method.

Introduction

Modern ultrafast experimental techniques have driven a blooming growth of our ability to track the carrier dynamics with high spatio-temporal resolutions, including ultrafast electron diffraction, and different time-resolved pump-probe spectroscopies. However, an accurate first-principle description of carrier dynamics at the atomic level is still challenging, owing to the quantum mechanical nature and the complexity of systems under research. A first-principle method to directly simulate carrier transport is demandingly needed to interpret experimental observations, illustrate fundamentals, and provide insights for better performances.

Team



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Outlook

We have developed an efficient *ab initio* computational framework to describe the real-time excited carrier dynamics for large-scale systems and long-time processes. This method allows a direct probe of carrier dynamics at the atomic scale. Our next step is to implement many-body effects (such as exciton) into our calculation.

Ref: *J. Phys. Chem. Lett.*, 10, 6174 (2019).

APL Materials 8, 041115 (2020).

Acknowledgments

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Results, Highlights, and Accomplishments

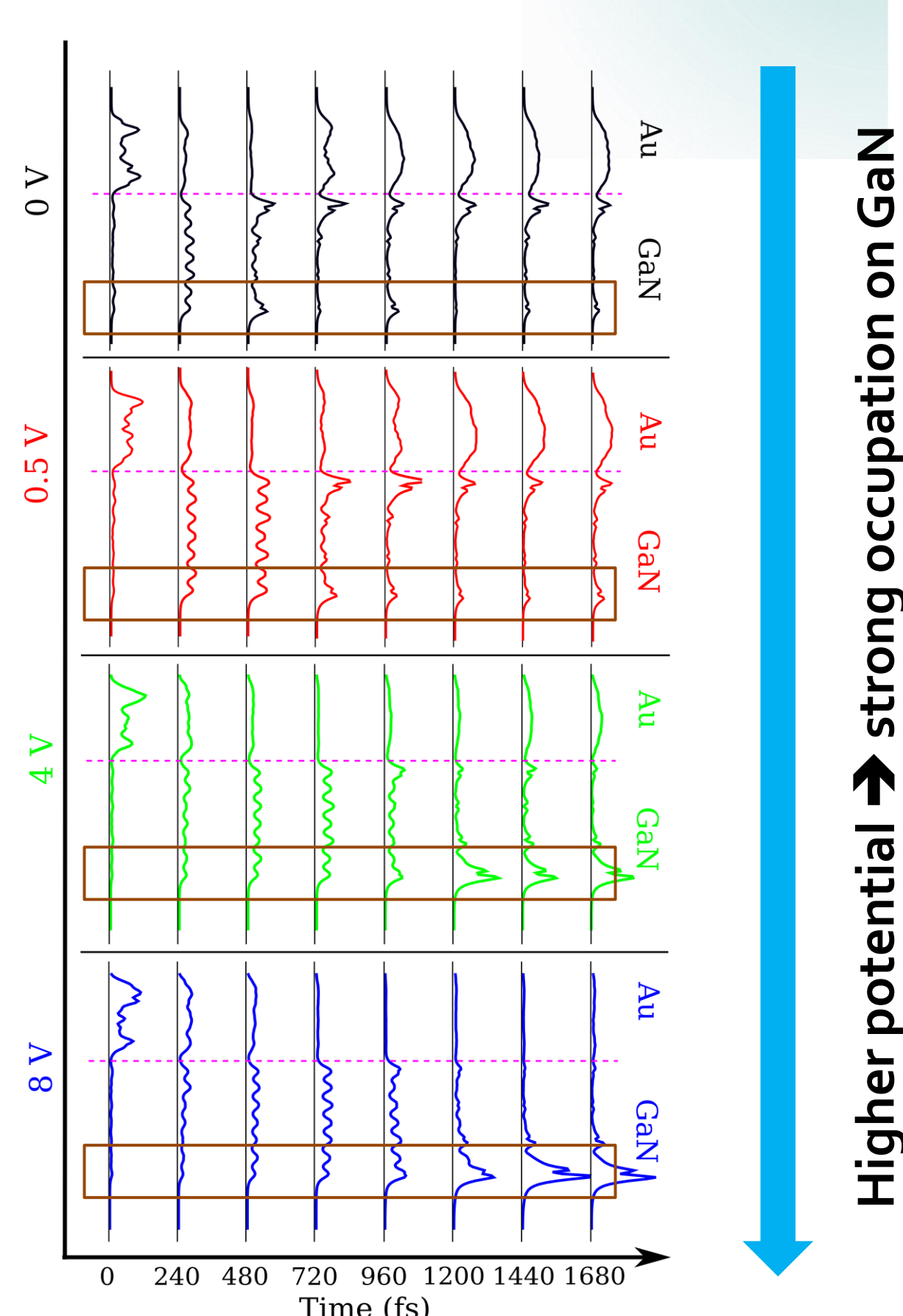
Reducing back-transfer in interfaces

GaN is widely used for the photoanode in CO₂ reduction. By simulating the hot hole transfer with NA-MD, a full profile of excited carriers is obtained.

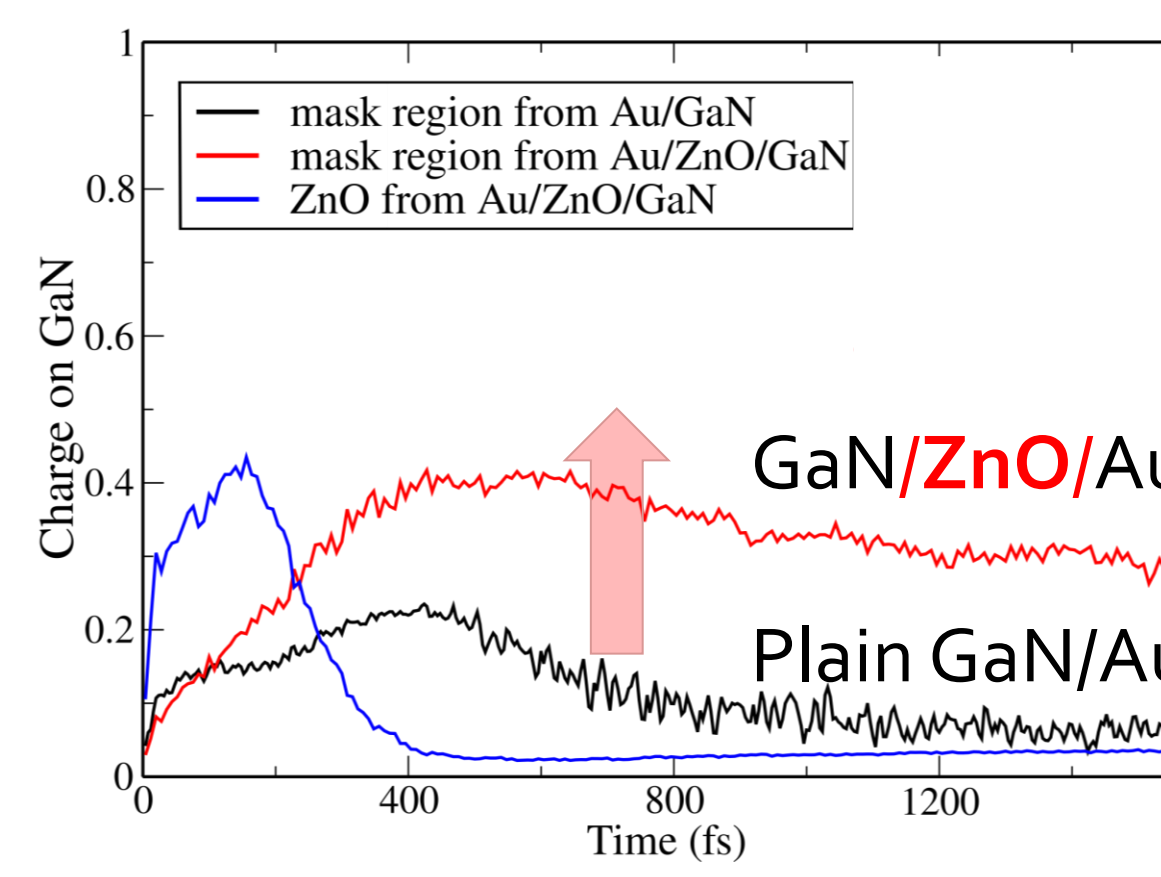
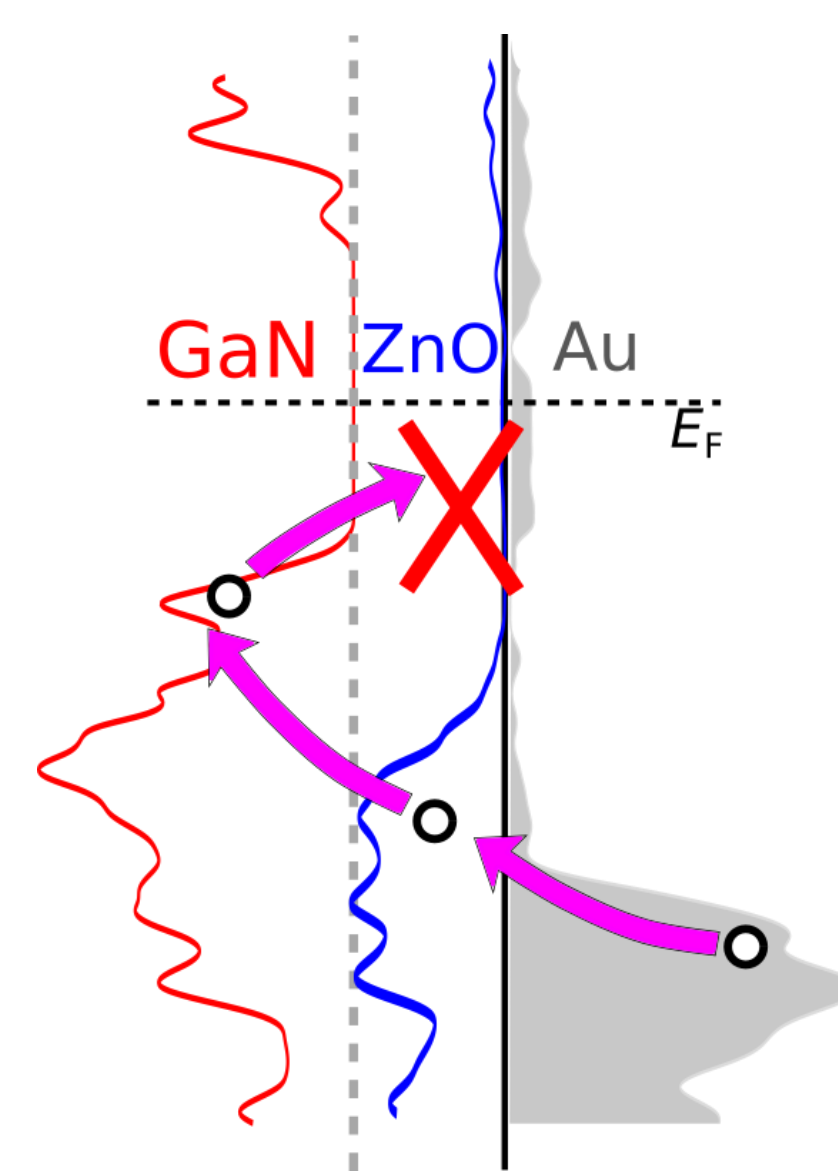
We find significant back-transfer which limits the charge separation. This back-transfer can be mitigated by the appropriate Schottky barrier and material/device design strategy.

• Schottky barrier

Applying different potential V to monitor how much charge can transfer to GaN instead of Au



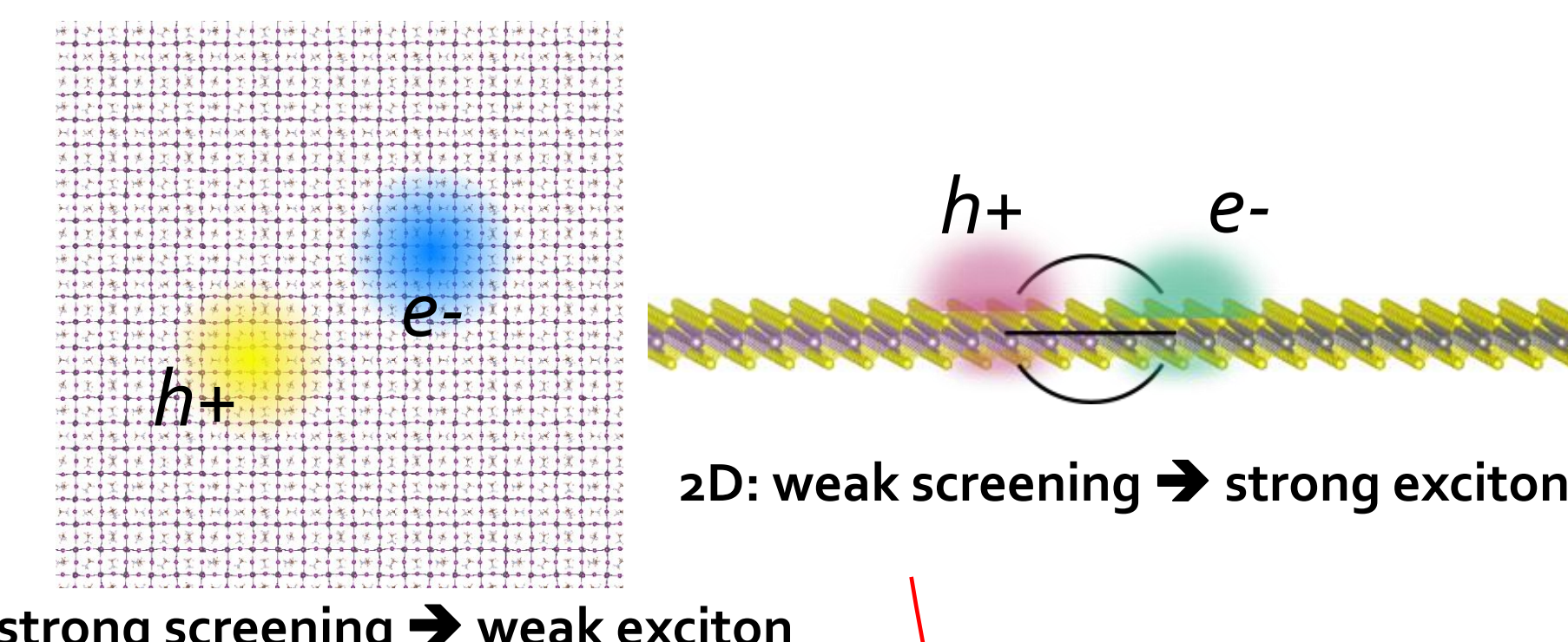
• Device design strategy -- ZnO



NA-MD with many-body effect

Current NA-MD is based on single-particle picture: carriers only have mean-field interaction inherited from DFT calculation. Many-body effects (such as exciton, polaron, et al) are included.

- As the most common quasi-particle, excitonic effect is weak in bulk material. But in low-dimensional materials, contribution of excitons is non-negligible.



- A screened Coulomb potential by electron (hole) charge is added to hole (electron) Hamiltonian

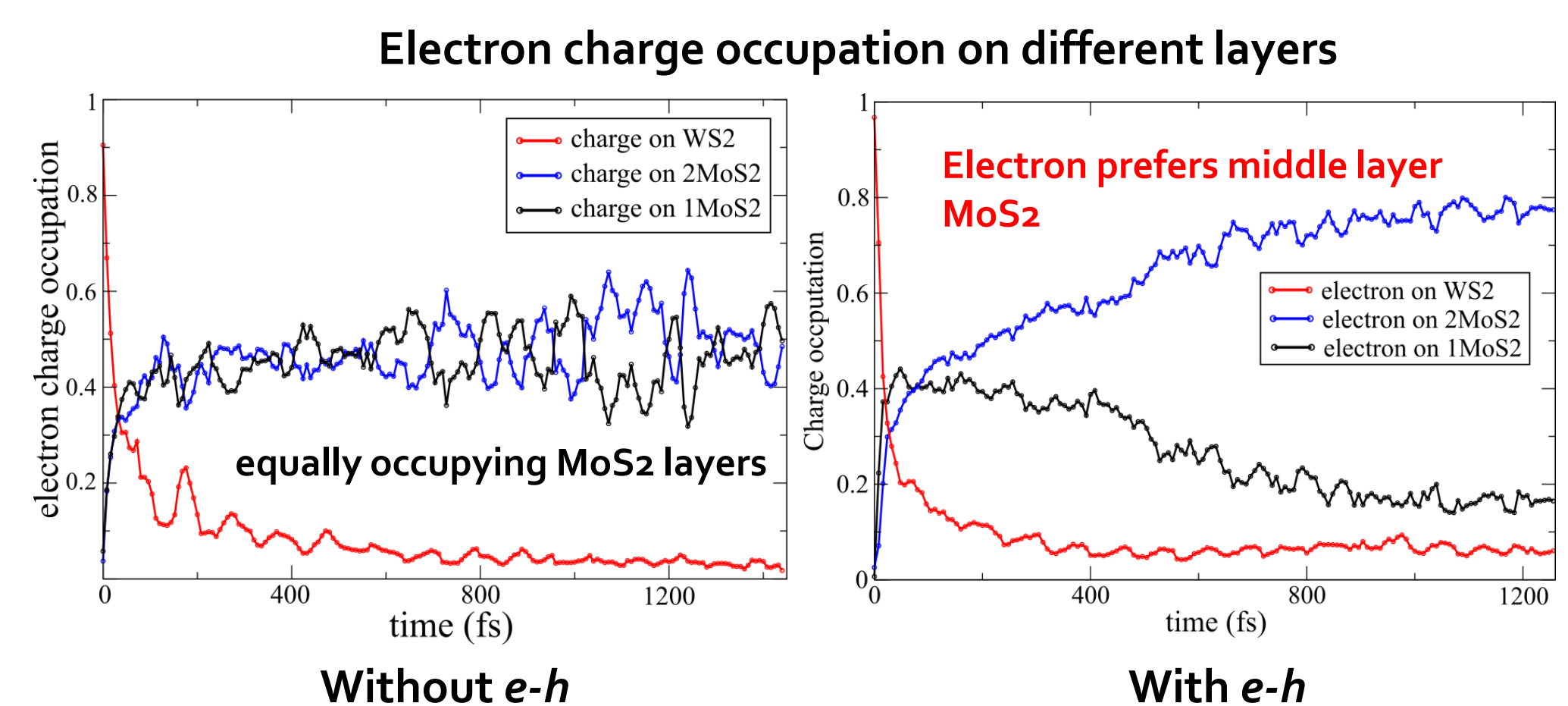
$$H^{(h)} = H_0^{(h)} - V[\rho(\mathbf{r}^{(e)})]$$

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Screened Coulomb potentials

- Decoherence induced surface hopping is implemented with satisfied detailed balance

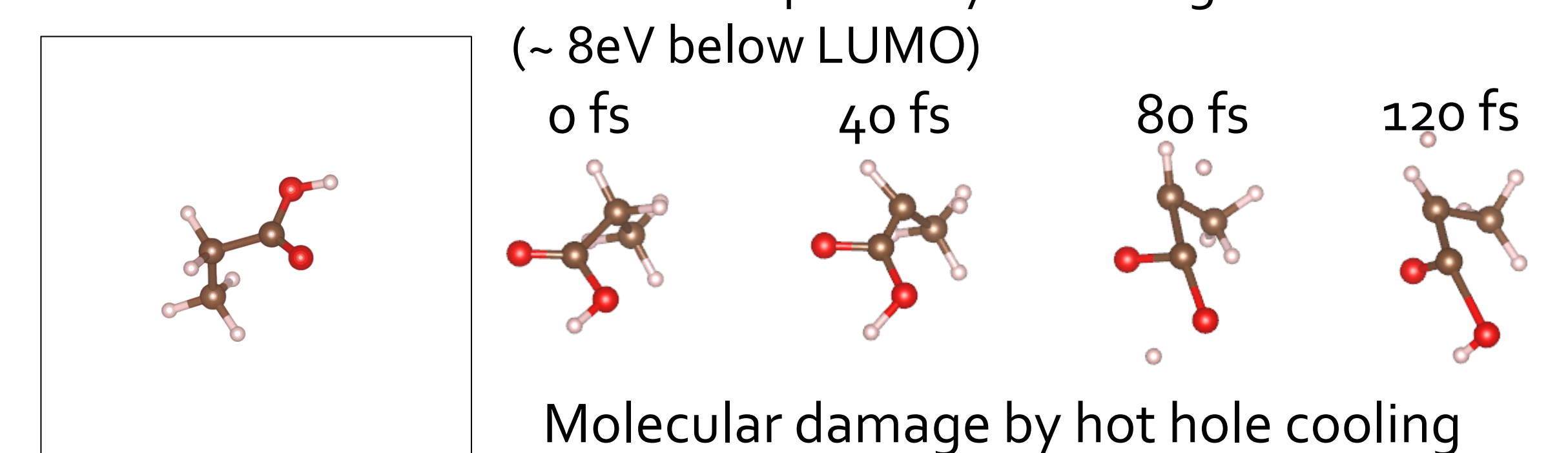
- Exciton dissociation in 2D heterostructures



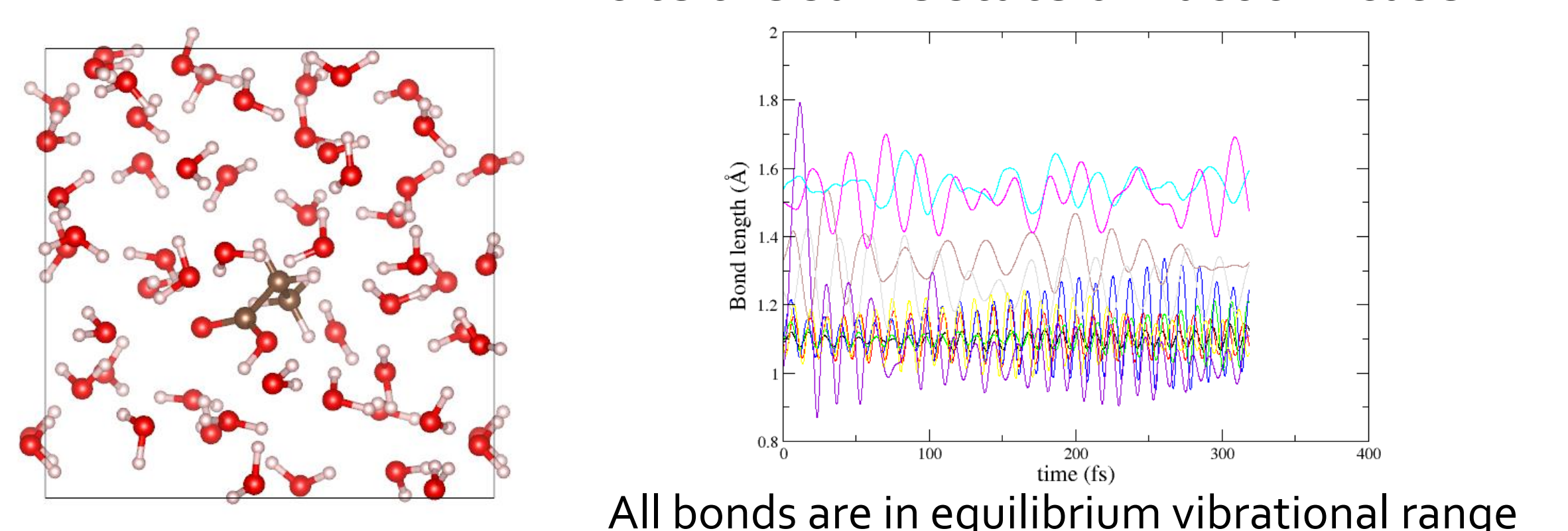
Hot carrier transfer under solvent condition

- We have developed wavefunction collapsing scheme to track how excited electrons contribute to ions' motion stochastically
- Our calculation shows that solvent can mitigate molecular damages caused by hot carriers

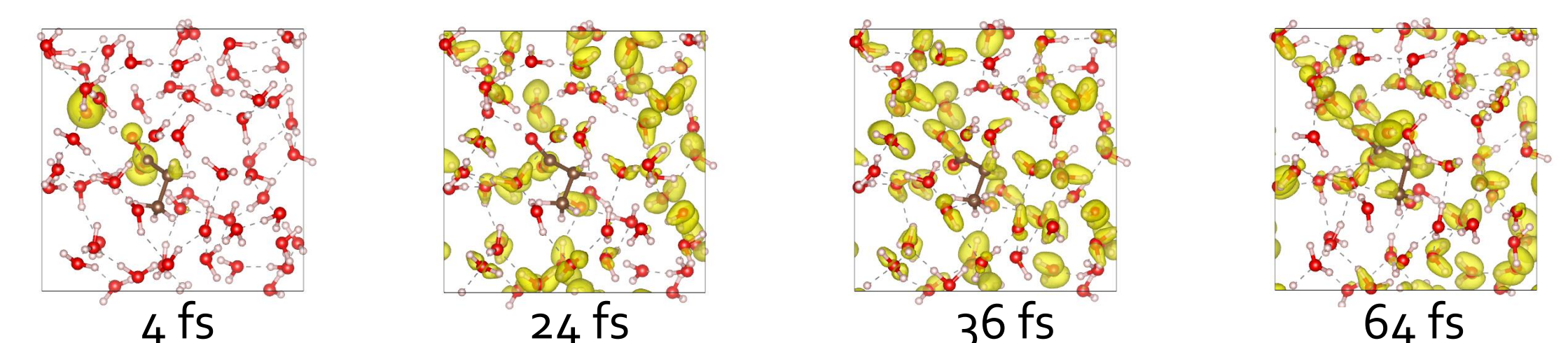
- In vacuum



- In solvent (water)



- Hot hole transfers from solute to solvent

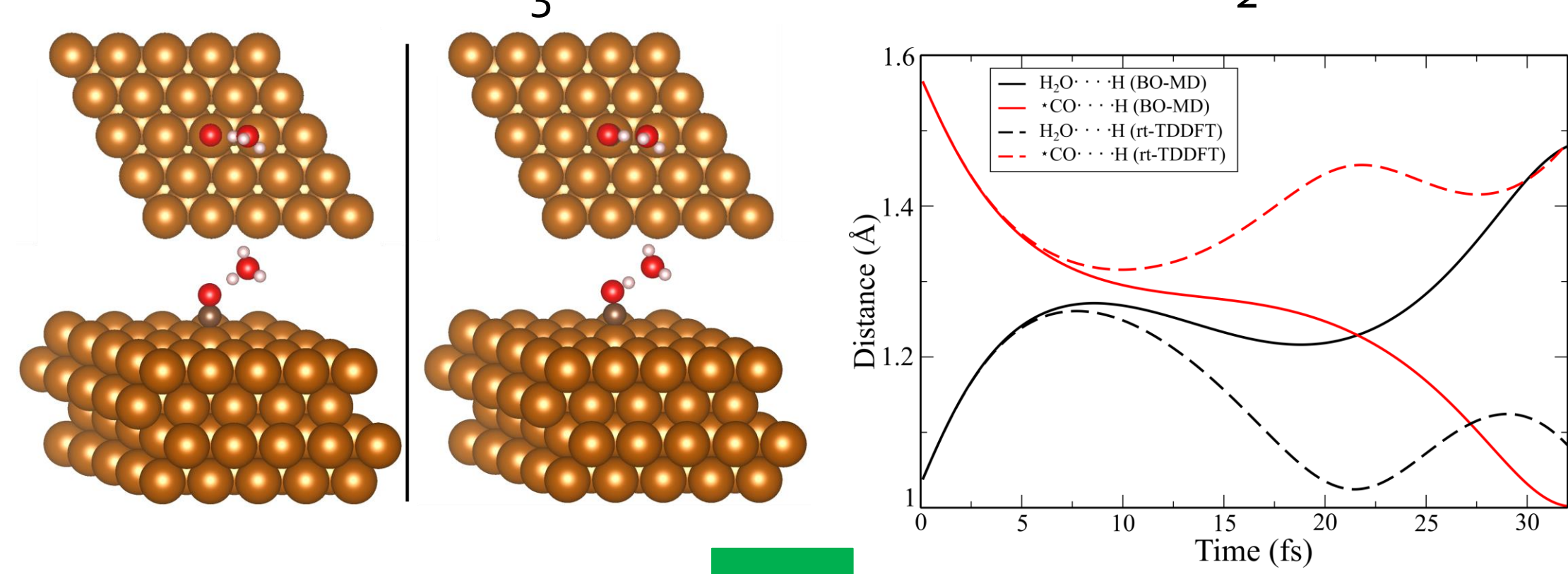
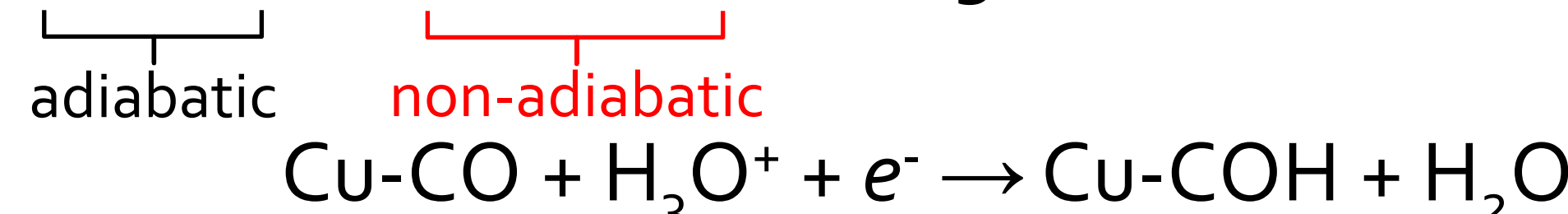


- Hot hole in solvent to heat water instead of damaging solute

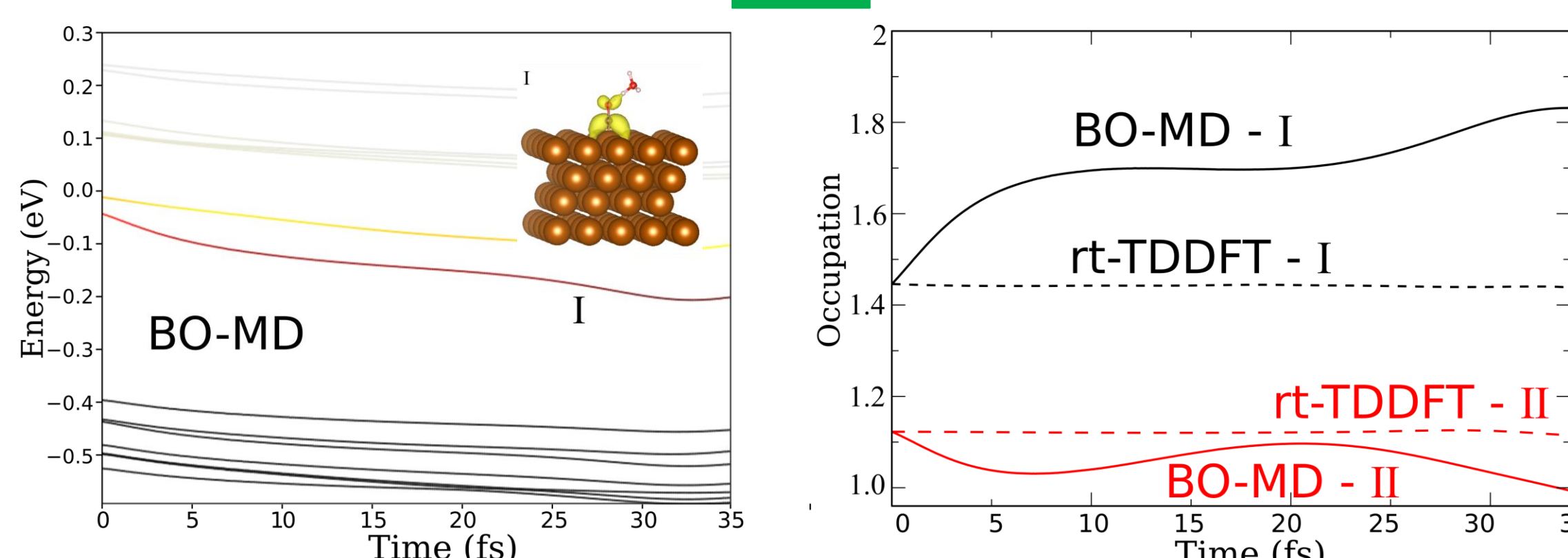
Non-adiabaticity in CO₂ reduction

- Using one step of CO₂ reduction as an example ...

BO-MD and rt-TDDFT starting from same initial condition



- BO-MD: reaction succeeds Yes**; **rt-TDDFT: reaction fails No**



rt-TDDFT predicts much slower occupation change of state-I than BO-MD
 → electron cannot transfer to proton and CO—H₃O bond breaking

- Reaction barriers with NA effect

Reaction Barrier (eV)	E_{NEB}	$E_{\text{BO-MD}}$	$E_{\text{rt-TDDFT}}$	$E_{\text{rt-TDDFT}} - E_{\text{BO-MD}}$ (meV)
Implicit solvent (add 2e ⁻)	0.080	0.196	0.208	12
Hybrid solvent (add 3e ⁻)	0.360	0.288	0.299	11
Hybrid solvent (add 4e ⁻)	0.411	0.363	0.373	10