THE UNIVERSITY of NORTH CAROLINA at CHAPEL HILL

VISTA seminar, June 12, 2024

Coupled Quantum Dynamics of Electrons and Protons in Heterogeneous Environments

Yosuke Kanai

Dept. Chemistry
Dept. Physics and Astronomy

University of North Carolina at Chapel Hill

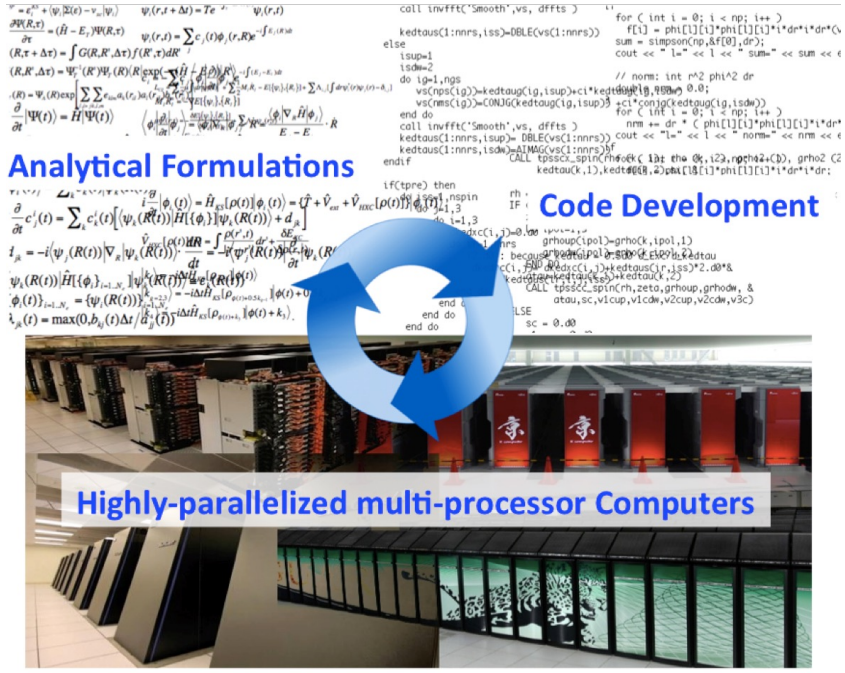
First-Principles Method Development for Condensed Matter

Real-time time-dependent density functional theory

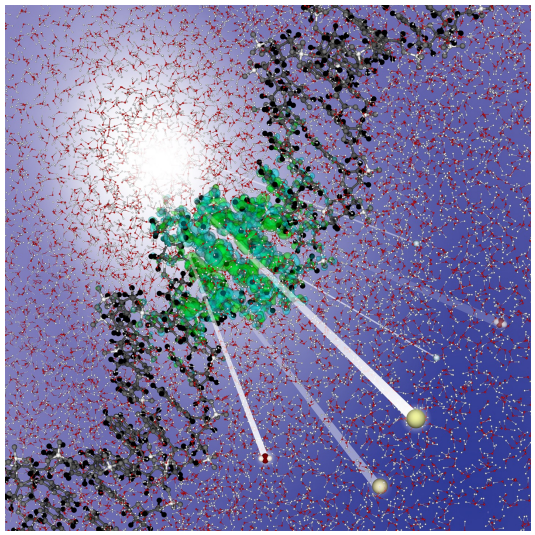
for non-equilibrium electron dynamics

Many-body Green's function theory

for electronic excitation properties



Phenomena of Current Interest

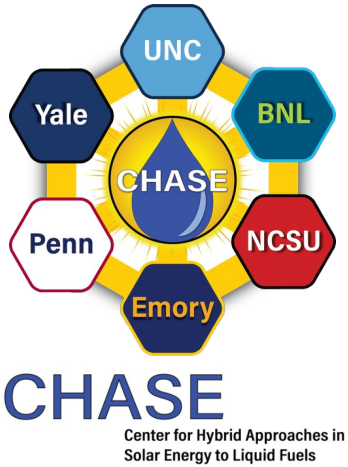


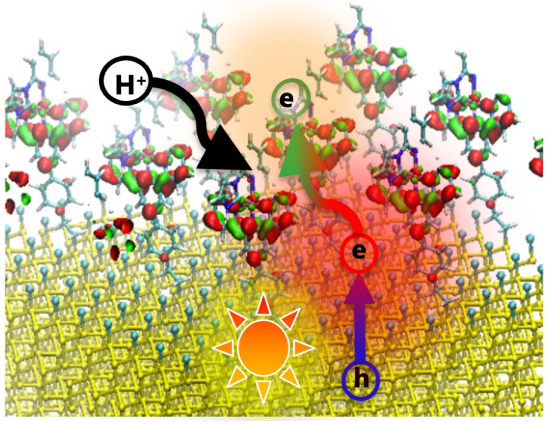
Electronic Stopping

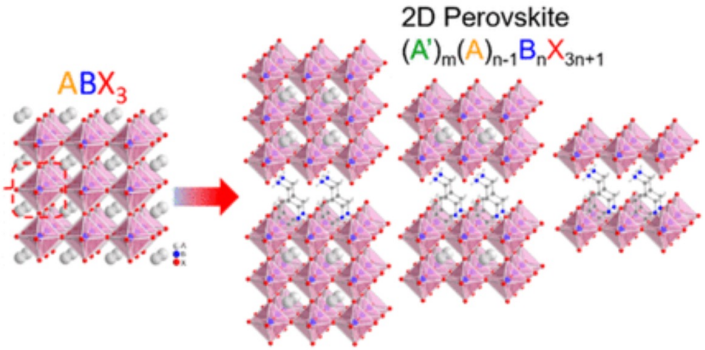
Excitation dynamics under proton irradiation and beyond

Quantum Dynamics of Electrons and Protons

Elucidating the mechanism for CO_2 conversion







Novel Materials and Dynamics

Application of first-principles method to "explore" interesting materials and dynamic phenomena

Kanai Group @ UNC

THE UNIVERSITY of NORTH CAROLINA at CHAPEL HILL

CHASE
Center for Hybrid Approaches in Solar Energy to Liquid Fuels

Dr. Jianhang Xu
Dr. Chris Shepard
Dr. Ruiyi Zhou
Sampreeti Bhattacharya
John Bost
Tom Carney
Nicolas Boyer
Kiichi Ogata

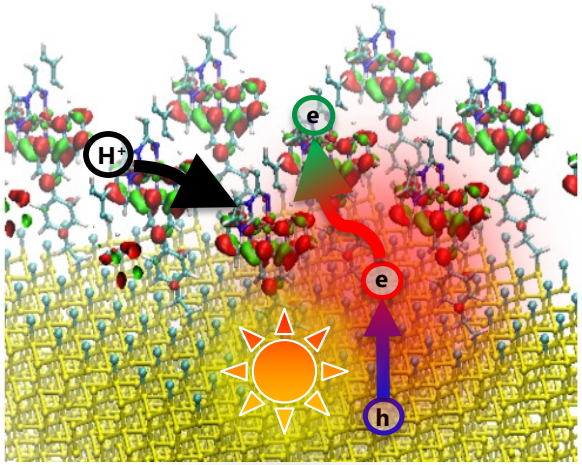
NSF

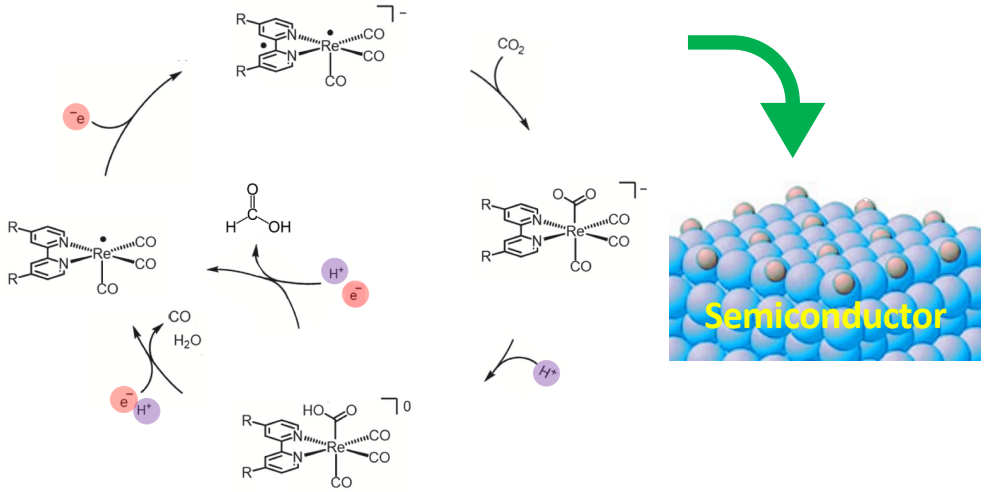
DEPARTMENT OF ENERGY · UNITED STATES OF AMERICA ·

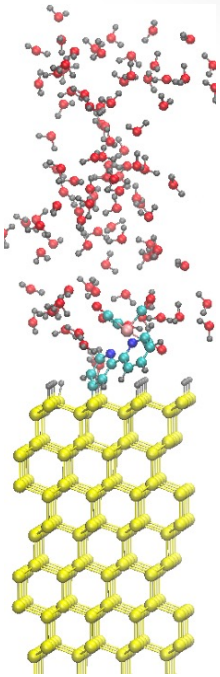
Theory Challenges in DOE Hub: CHASE

CHASE
Center for Hybrid Approaches in Solar Energy to Liquid Fuels

Development of CO_2-catalyst functionalized semiconductor photoelectrodes







How does surface adsorption impact H^+/e^- transfer steps?

Complex heterogeneous environments need to be modeled.

To what extent is the interfacial excited e^- transfer coupled with H^+ addition at an interface?

Coupled quantum dynamics of protons and electrons need to be considered.

NEO to KS-DFT for Periodic Systems

FHI-aims
The ab initio materials simulation package

Multicomponent DFT

$$E[\rho^{\mathrm{e}}, \rho^{\mathrm{p}}] = E_{\mathrm{ref}}[\rho^{\mathrm{e}}, \rho^{\mathrm{p}}] + E_{XC}^{e}[\rho^{\mathrm{e}}] + E_{XC}^{p}[\rho^{\mathrm{p}}] + E_{epc}[\rho^{\mathrm{e}}, \rho^{\mathrm{p}}]$$

"Non-Born–Oppenheimer Density Functional Theory of Molecular Systems"

J. F. Capitani, R. F. Nalewajski, and R. G. Parr, J. Chem. Phys. 76, 568 (1982)

"Multicomponent Density-Functional Theory for Electrons and Nuclei"

T. Kreibich and E. K. U. Gross, Phys. Rev. Lett. 86, 2984 (2001)

Nuclear Electronic Orbital (NEO) method

F. Pavosevic, T. Culpitt, S. Hammes-Schiffer, Chem. Rev. **120**, 4222 (2020)

NEO to KS-DFT for periodic systems

J. Xu, R. Zhou, Z. Tao, C. Malbon, V. Blum, S. Hammes-Schiffer, Y. Kanai, J. Chem. Phys. 156, 224111 (2022)

$$\psi_{i,\mathbf{k}}^{e}(\mathbf{r}^{e}) = \sum_{\mu} c_{i\mu,\mathbf{k}} \sum_{N} e^{i\mathbf{k}\cdot\mathbf{T}(\mathbf{N})} \phi_{\mu}^{e:NAO/GTO}\left(\mathbf{r}^{e} - \mathbf{R}_{\mu} + \mathbf{T}(\mathbf{N})\right)$$

$$\psi_{i}^{p}(\mathbf{r}^{p}) = \sum_{m} c_{im} \sum_{N} \phi_{m}^{p:GTO}\left(\mathbf{r}^{p} - \mathbf{R}_{m} + \mathbf{T}(\mathbf{N})\right)$$

Atom-centered basis functions

FHI-aims
The ab initio materials simulation package

KS Hamiltonian in Multicomponent DFT

$$\hat{H}^e_{KS} = -\frac{1}{2}\nabla_e^2 + v_{ext}(\mathbf{r}^e) + v^e_{es}(\mathbf{r}^e) - v^p_{es}(\mathbf{r}^e) + \frac{\delta E^e_{XC}[\rho^e]}{\delta \rho^e} + \frac{\delta E_{epc}[\rho^e, \rho^p]}{\delta \rho^e}$$

$$\hat{H}^p_{KS} = -\frac{1}{2M^p}\nabla_p^2 - v_{ext}(\mathbf{r}^p) - v^e_{es}(\mathbf{r}^p) + v^p_{es}(\mathbf{r}^p) + \frac{\delta E^p_{XC}[\rho^p]}{\delta \rho^p} + \frac{\delta E_{epc}[\rho^e, \rho^p]}{\delta \rho^p}$$

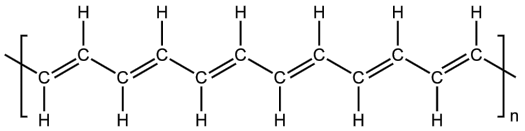
Electron-Proton Correlation

Multicomponent extensions of **Colle−Salvetti formalism** have been developed. The simplest form is the local density approximation (LDA)

Y. Yang, et al., J. Chem. Phys. **147**, 114113 (2017)

$$E_{epc}[\rho^e, \rho^p] \approx E_{epc17-2}[\rho^e, \rho^p] = -\int \frac{\rho^e(\boldsymbol{r})\rho^p(\boldsymbol{r})}{a + b\rho^e(\boldsymbol{r})^{\frac{1}{2}}\rho^p(\boldsymbol{r})^{\frac{1}{2}} + c\rho^e(\boldsymbol{r})\rho^p(\boldsymbol{r})} d\boldsymbol{r}$$

Proof-of-Principle Demonstration



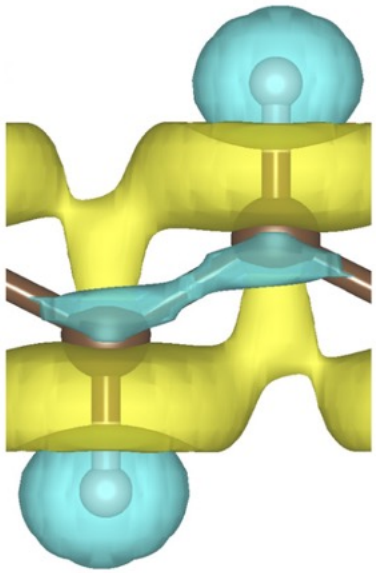
NEO-induced Electron Density difference

(+) change

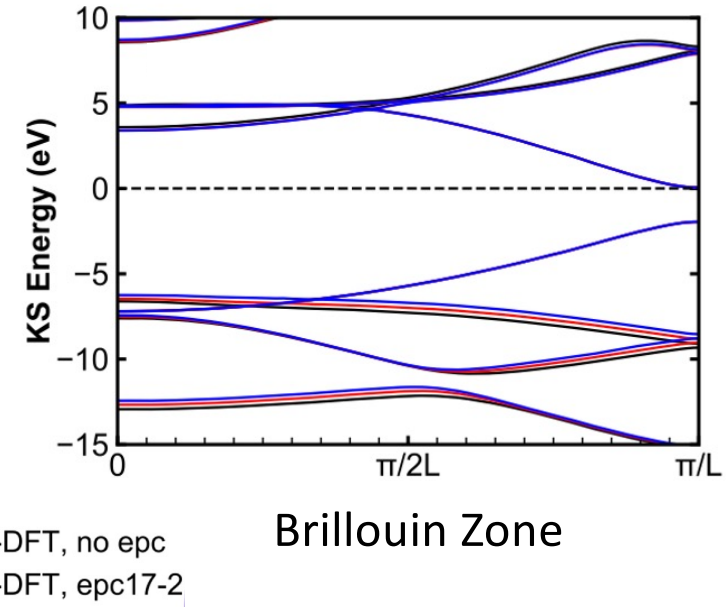
(-) change

Isosurface @ 1.7 x 10^{-2} Ang^{-3}

$\Delta\rho^e(\mathbf{r})$

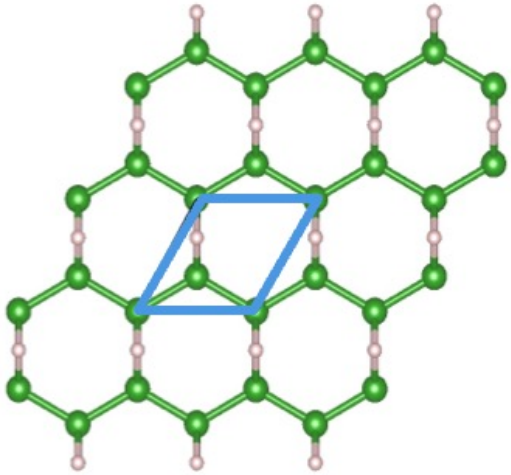


Band Structure

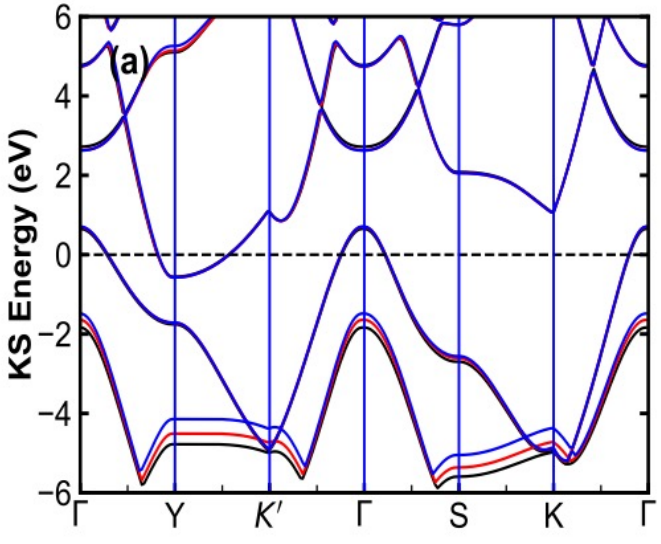


Brillouin Zone

Hydrogen Boride 1D sheet : B-H-B 3-center-2-electron bonds



Y. Jiao, et al. Angewandte Chemie, 55, 35 (2016)



DFT

NEO-DFT w/o epc

NEO-DFT w/ epc

Dynamics : Lagrangian for our NEO DFT-KS System

$$L^{NEO}(t) = \int d\mathbf{r}^e \int d\mathbf{k} \sum_{\mathbf{j}} [\psi^e_{\mathbf{jk}}(\mathbf{r}^e,t)]^* \left[i\frac{\partial}{\partial t} + \frac{1}{2m^e}\nabla^2_{\mathbf{r}^e} \right] \psi^e_{\mathbf{jk}}(\mathbf{r}^e,t)$$

$$- \frac{1}{2}\iint d\mathbf{r}^e\, d\mathbf{r}^{e\prime} \frac{e^2}{|\mathbf{r}^e - \mathbf{r}^{e\prime}|} \rho^e(\mathbf{r}^e,t)\rho^e(\mathbf{r}^{e\prime},t) - E^e_{XC}[\rho^e]$$

$$+ \int d\mathbf{r}^p \sum_{\mathbf{j}} [\psi^p_j(\mathbf{r}^p,t)]^* \left[i\frac{\partial}{\partial t} + \frac{1}{2M^p}\nabla^2_{\mathbf{r}^p} \right] \psi^p_j(\mathbf{r}^p,t)$$

$$- \frac{1}{2}\iint d\mathbf{r}^p\, d\mathbf{r}^{p\prime} \frac{e^2}{|\mathbf{r}^p - \mathbf{r}^{p\prime}|} \rho^p(\mathbf{r}^p,t)\rho^p(\mathbf{r}^{p\prime},t) - E^p_{XC}[\rho^p]$$

$$+ \frac{1}{2}\iint d\mathbf{r}^e\, d\mathbf{r}^p \frac{e^2}{|\mathbf{r}^e - \mathbf{r}^p|} \rho^e(\mathbf{r}^e,t)\rho^p(\mathbf{r}^p,t) - E_{epc}[\rho^e,\rho^p]$$

$$+ \sum_I \frac{1}{2} M_I \left[\dot{\boldsymbol{R}}_I(t)\right]^2 - \sum_{I<J} \frac{Z_I Z_J e^2}{|\boldsymbol{R}_I(t) - \boldsymbol{R}_J(t)|}$$

$$- \int d\mathbf{r}^p\, \rho^p(\mathbf{r}^p,t) \sum_I \frac{Z_I e^2}{|\mathbf{r}^p - \boldsymbol{R}_I(t)|} + \int d\mathbf{r}^e\, \rho^e(\mathbf{r}^e,t) \sum_I \frac{Z_I e^2}{|\mathbf{r}^e - \boldsymbol{R}_I(t)|}$$

TD-KS equations for RT-NEO-TDDFT

$$A = \int L^{NEO}\left(\mathbf{R}, \dot{\mathbf{R}}, \{\psi^e_{i,\mathbf{k}}\}, \{\psi^p_I\}, t\right) dt \qquad \frac{\delta A}{\langle \delta\psi^x |} = 0 \qquad \frac{\delta L^{NEO}}{\langle \delta\psi^x |} - \frac{d}{dt}\frac{\delta L^{NEO}}{\langle \delta\dot{\psi}^x |} = 0$$

See. e.g. Kramer and Saraceno, "Geometry of the Time-Dependent Variational Principle" (Springer, Berlin, 1981).

Electrons: $$i\frac{\partial}{\partial t}\psi^e_{i,\mathbf{k}}(\mathbf{r}^{\mathrm{e}}, t) = \left[-\frac{1}{2}\nabla_i^2 + v^e_{\mathrm{DFT-KS}}(\mathbf{r}^{\mathbf{e}}) - v^p_{\mathrm{es}}(\mathbf{r}^{\mathrm{e}}) + \frac{\delta E_{\mathrm{epc}}[\rho^{\mathrm{e}}, \rho^{\mathrm{p}}]}{\delta \rho^e}\right]\psi^e_{i,\mathbf{k}}(\mathbf{r}^{\mathrm{e}}, t)$$

RT-TDDFT **All-electron real-time and imaginary-time TDDFT within a numeric atom-centered basis function framework** J. Hekele, et al. J. Chem. Phys. 155, 154801 (2021)

Protons: $$i\frac{\partial}{\partial t}\psi^p_I(\mathbf{r}^{\mathrm{p}}, t) = \left[-\frac{1}{2M^p}\nabla_I^2 + v^p_{\mathrm{DFT-KS}}(\mathbf{r}^{\mathrm{p}}) - v^e_{\mathrm{es}}(\mathbf{r}^{\mathrm{p}}) + \frac{\delta E_{\mathrm{epc}}[\rho^{\mathrm{e}}, \rho^{\mathrm{p}}]}{\delta \rho^p}\right]\psi^p_I(\mathbf{r}^{\mathrm{p}}, t)$$

L. Zhao, et al., J. Phys. Chem. Lett. **11**, 4052 (2020)

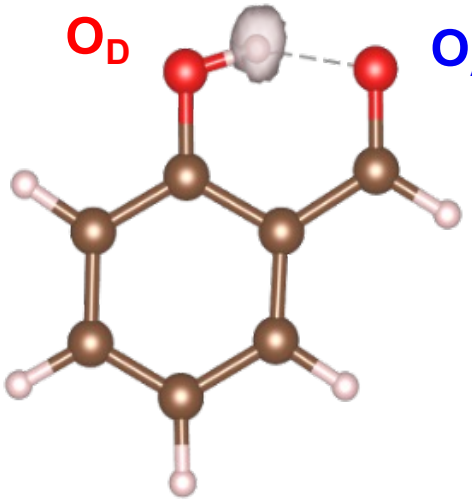
$$\psi^p_i(\mathbf{r}^p, t) = \sum_m c_{im}(t) \sum_N \phi^{p:GTO}_m\left(\mathbf{r}^p - \mathbf{R}_m + \mathbf{T}(\mathbf{N})\right)$$

$$\mathbf{C}(t + \Delta t) = \mathbf{S}^{-\frac{1}{2}} \exp\left(-i\Delta t \mathbf{S}^{-\frac{1}{2}} \mathbf{H}_{\boldsymbol{KS}}\left(t + \tfrac{\Delta t}{2}\right)\mathbf{S}^{-\frac{1}{2}}\right)\mathbf{S}^{\frac{1}{2}}\mathbf{C}(t)$$

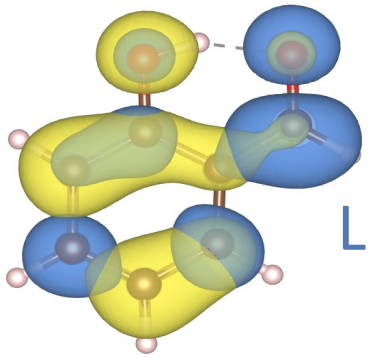
$$\exp(\mathbf{A}) = \mathbf{V}\mathrm{diag}\left(e^{\lambda_1}, e^{\lambda_2} \ldots e^{\lambda_n}\right)\mathbf{V}^{-1}$$

Electronic Excitation Induced Intra-Molecular Proton Transfer

oHBA molecule

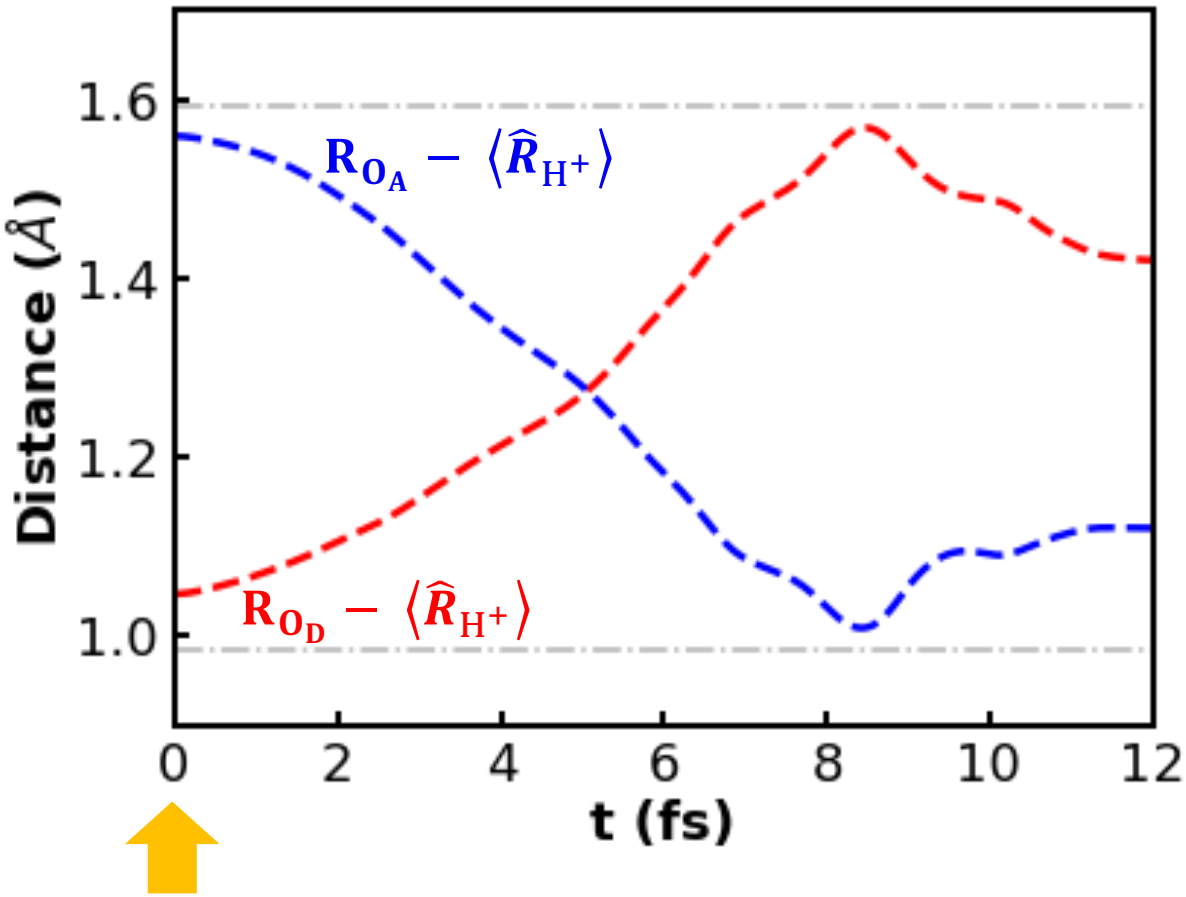


HOMO



LUMO

Electrons: PBE + Tier2 NAO basis
Protons: HF + 4s4p basis w/ 3 "ghost" centers
EPC: epc-17-2 , dt=4.8 attosecs

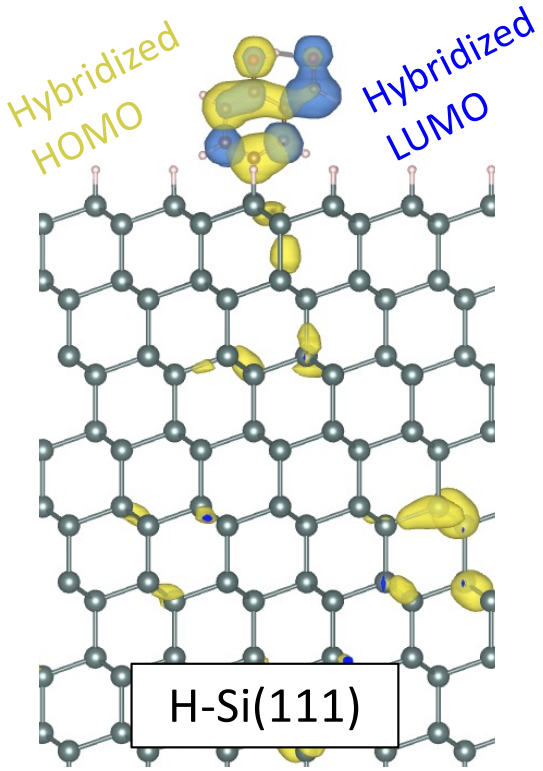


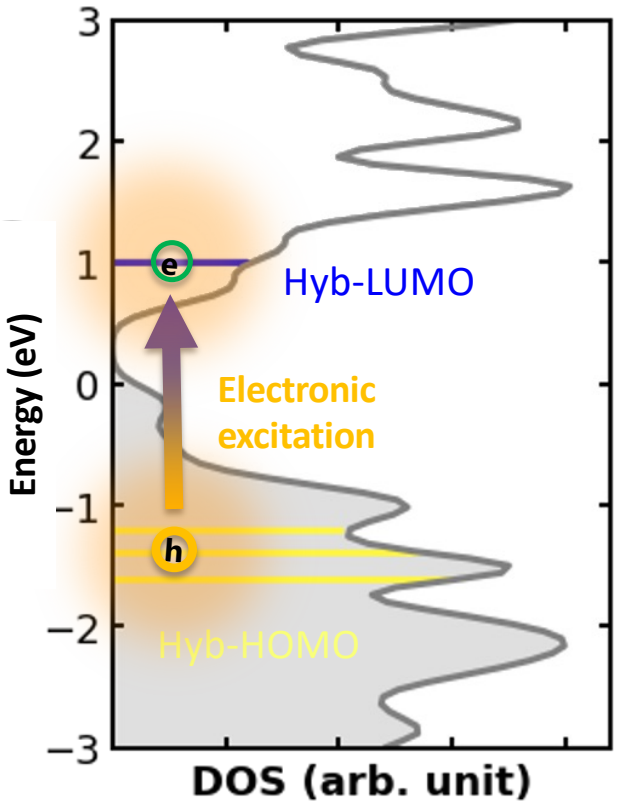
Electronic Excitation (HOMO → LUMO)

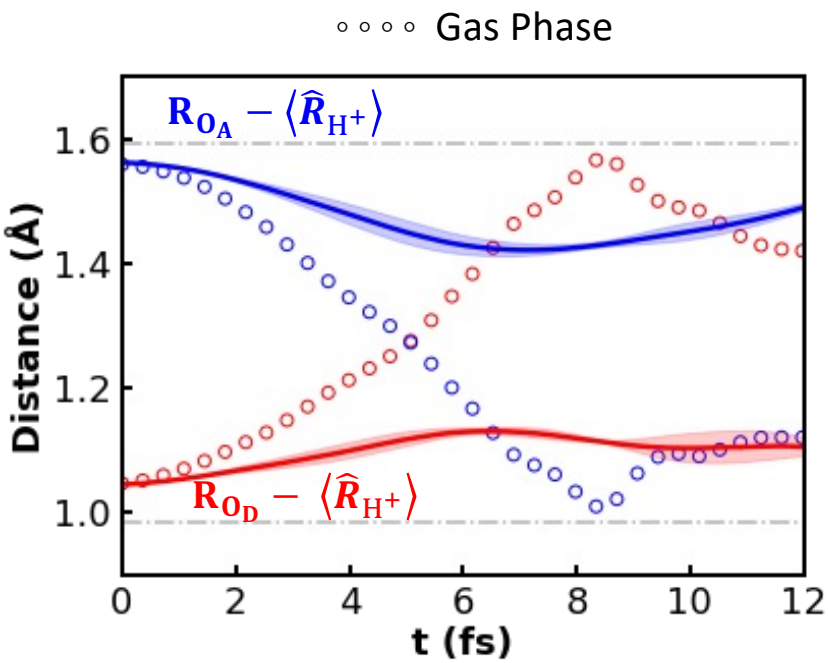
L. Zhao, et al., J. Phys. Chem. Lett. **11**, 4052 (2020)

oHBA attached on Semiconductor Surface

oHBA





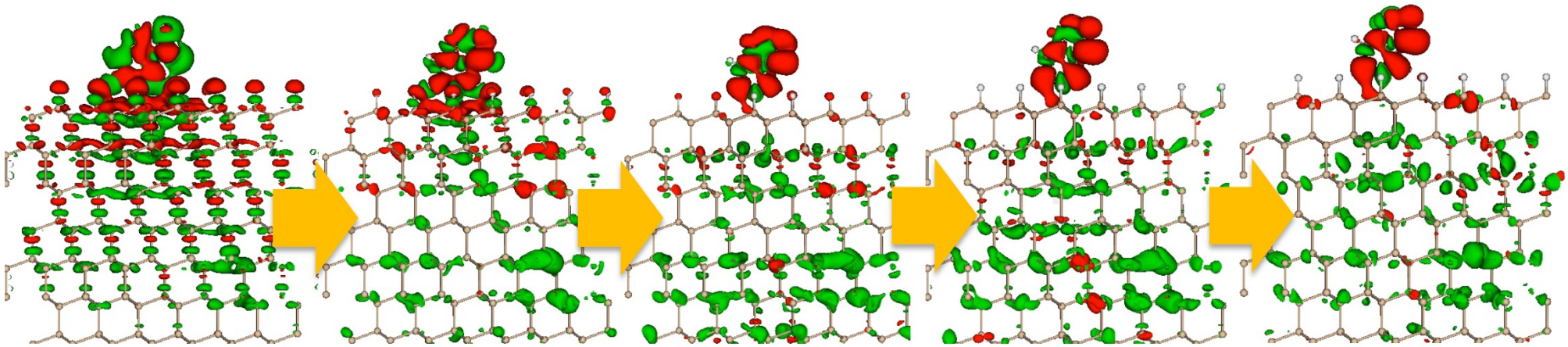


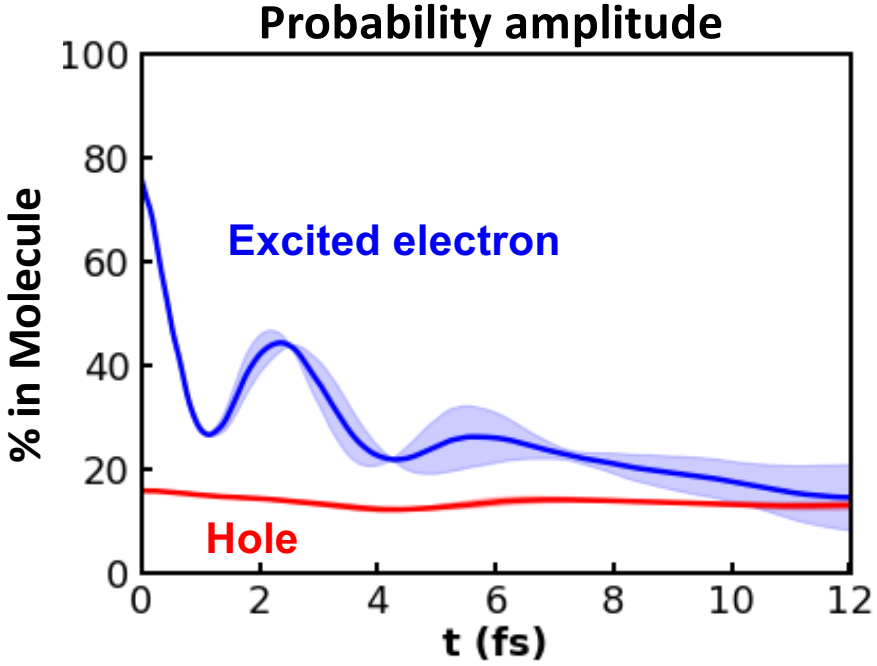
~3700 electrons.

H^+ transfer does NOT take place!

Electron Density Changes at Interface

Electron density change : $\Delta\rho^e(\mathbf{r},t)$ Increases / Decreases

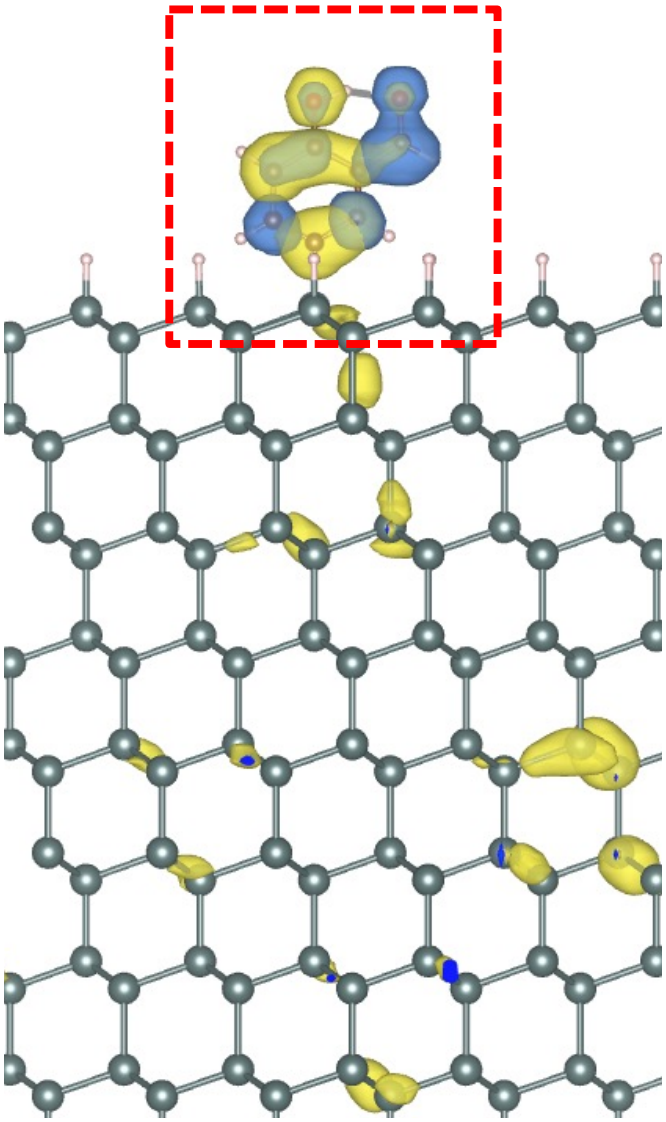


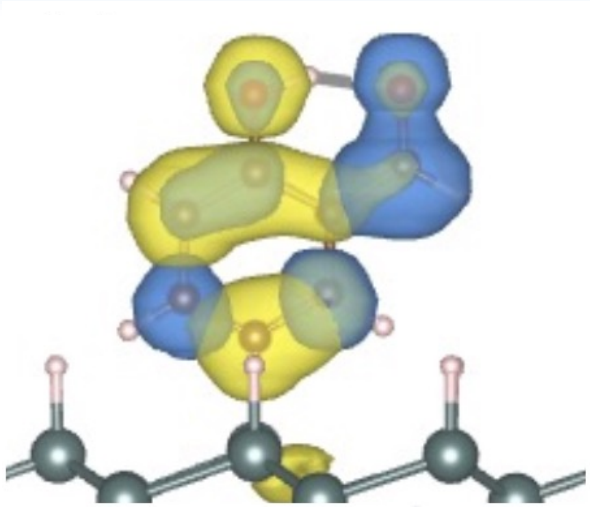


Ultrafast transfer of excited electron to semiconductor surface.

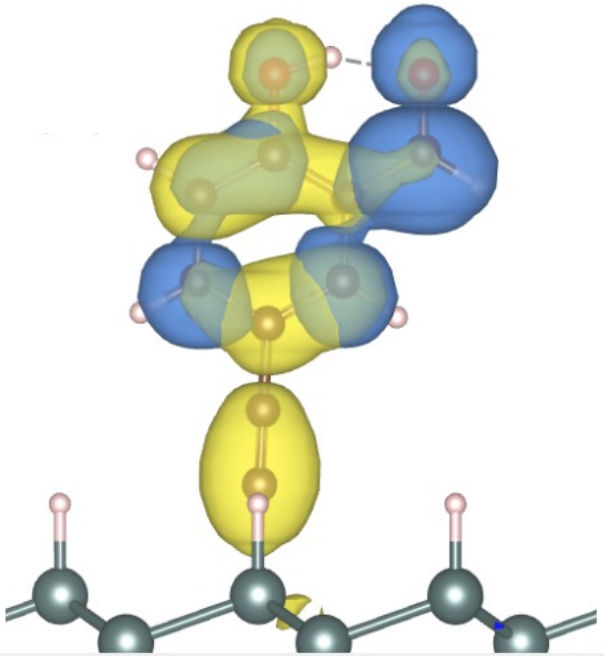
No driving force for the intra-molecular H^+ transfer.

Role of Excited Electron Transfer

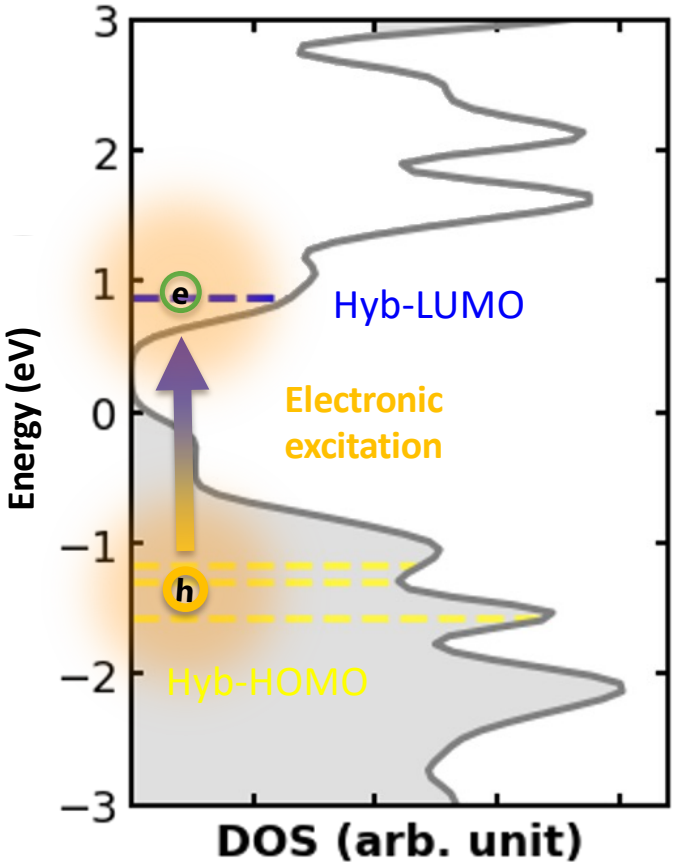


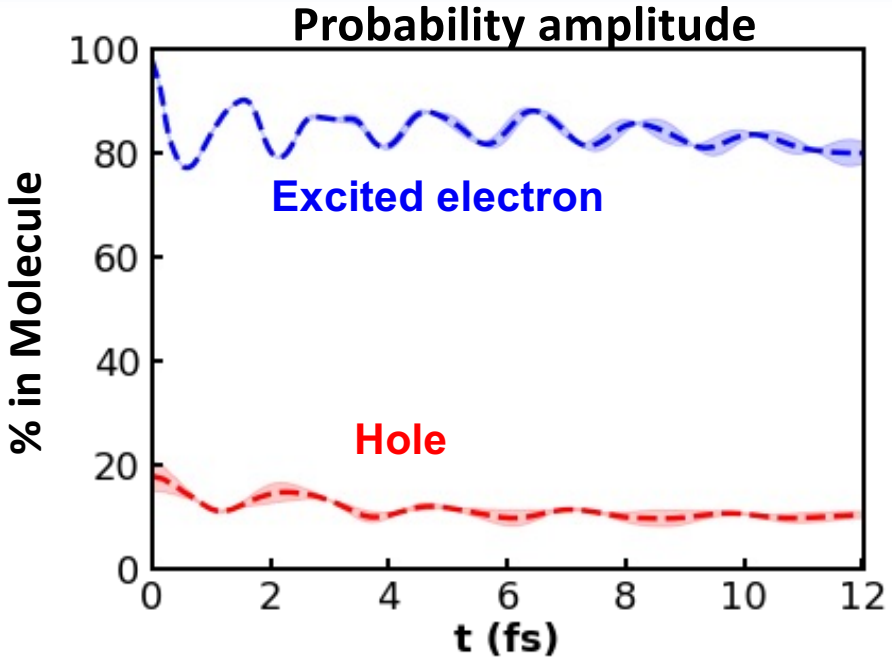


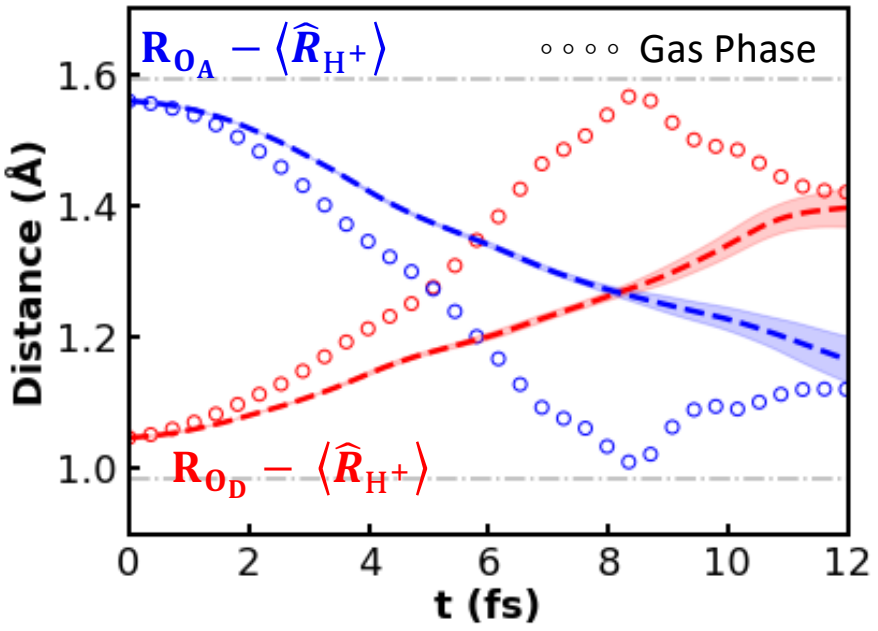
$-\mathbf{C} \equiv \mathbf{C} -$ **Linker**



Controlling Electron Transfer w/ Linker Group



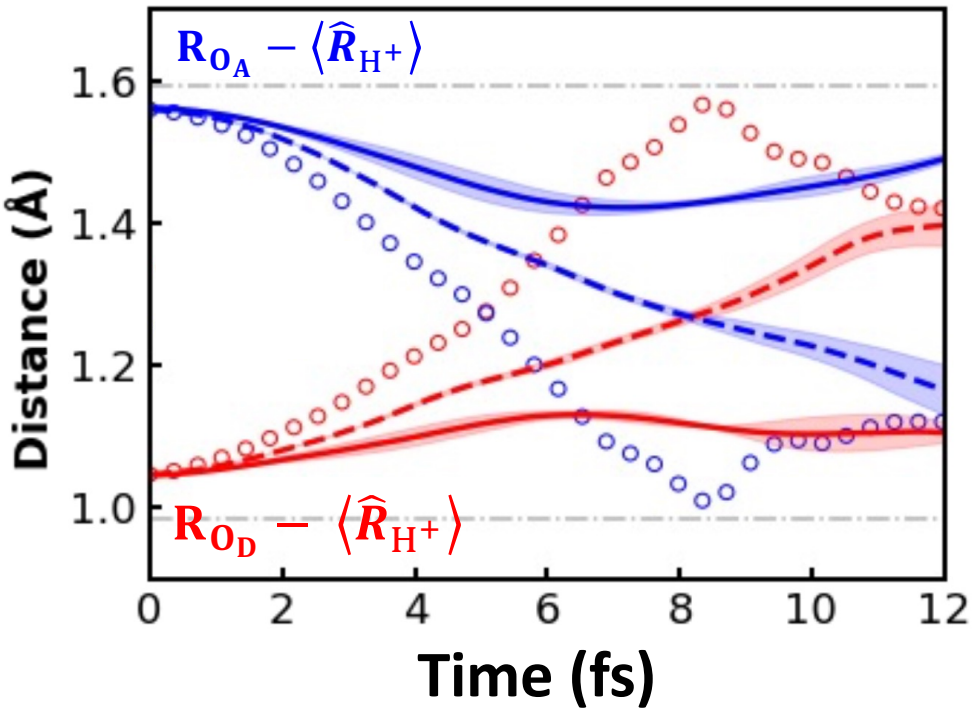


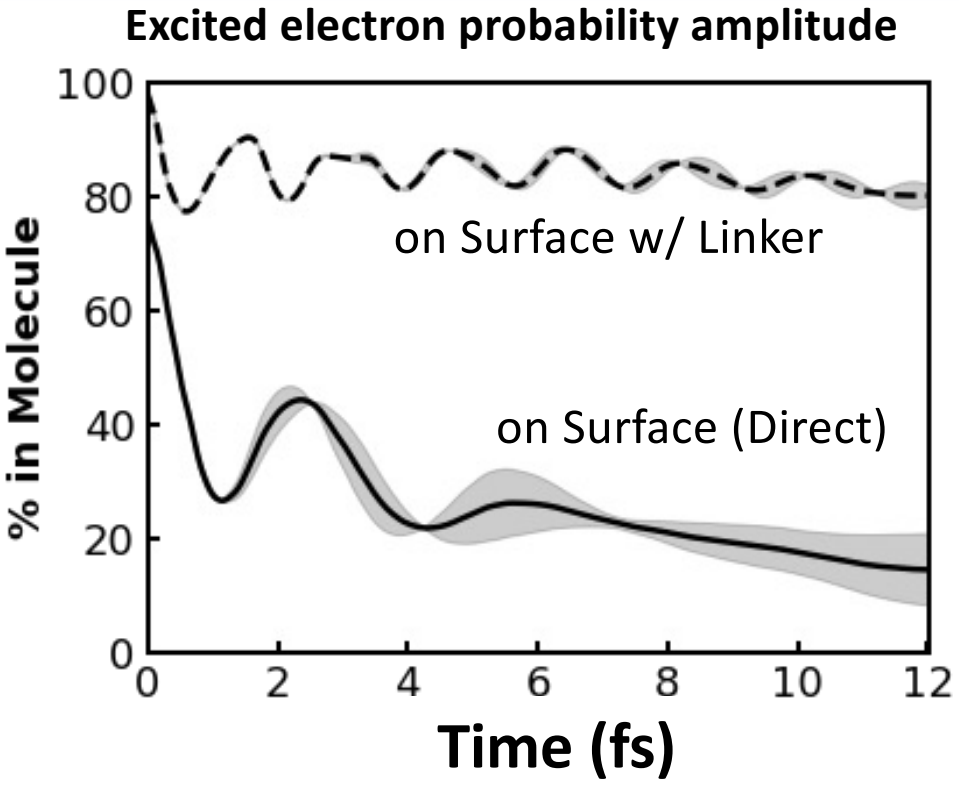


Excited electron transfer to the semiconductor is significantly slower with the linker group.

Excitation-induced H^+ transfer takes place!

Dependence on the surface attachment



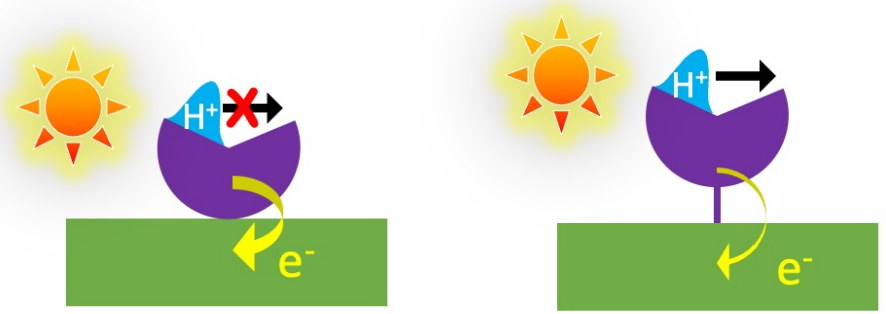


Gas Phase

on Surface (Direct)

on Surface w/ Linker

Surface attachment controls intra-molecular H^+ transfer via interfacial excited electron transfer.



Summary and References

NEO-DFT method for periodic systems.

Nuclear-Electronic Orbital Approach to Quantization of Protons in Periodic Electronic Structure Calculations
J. Xu, R. Zhou, Z. Tao, C. Malbon, V. Blum, S. Hammes-Schiffer, Y. Kanai
J. Chem. Phys. 156, 224111 (2022)

RT-TDDFT Implementation in all-electron periodic systems with NAO basis.

All-electron real-time and imaginary-time time-dependent density functional theory within a numeric atom-centered basis function framework
J. Hekele, Y. Yao, Y. Kanai, V. Blum, P. Kratzer
J. Chem. Phys. 155, 154801 (2021)

Periodic RT-NEO-TDDFT method for studying coupled electron-proton dynamics in heterogeneous systems

First-Principles Approach to Coupled Quantum Dynamics of Electrons and Protons in Heterogeneous Systems
J. Xu, R. Zhou, V. Blum, T. E. Li, S. Hammes-Schiffer, Y. Kanai
Phys. Rev. Lett. 131, 238002 (2023) Editors' Suggestion

Ehrenfest dynamics extension using Lagrangian formulation for traveling proton basis scheme

Lagrangian Formulation of RT-NEO-TDDFT Ehrenfest Dynamics (temp)
J. Xu, R. Zhou, T. E. Li, S. Hammes-Schiffer, Y. Kanai
In preparation

Thank you for listening!