

CHASE: SOLAR ENERGY CONVERSION WITH MOLECULAR-SEMICONDUCTOR HYBRIDS

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The quest for hybrid photoelectrodes that efficiently upgrade abundant feedstocks to high energy fuels that can be stored is of critical importance. Recently a Solar Hub entitled the **Center for Hybrid Approaches in Solar Energy to Liquid Fuels**, or CHASE, was funded by the US Department of Energy to advance the fundamental science necessary to realize hybrid photoelectrodes based on molecular catalysts integrated with semiconducting electrodes, see: <https://chaseliquidfuels.org/> This presentation will focus on the mechanisms of fundamental electron transfer and proton coupled electron transfer (PCET) reactions [1,2]. Particular attention is placed on the location of molecular catalysts within the electric double layer and the impact of strong electronic coupling on light initiated interfacial electron transfer.

Interfacial electron transfer kinetics to catalysts positioned about 4-20 Å from a conductive oxide surface were measured as a function of the thermodynamic driving force [3]. Marcus-Gerischer analysis of this data revealed a dramatically reduced electron transfer barrier for catalysts located within the Helmholtz planes suggesting that outer-sphere reorganization was absent. The analysis is fully consistent with a greatly reduced solvent dielectric constant and a tremendous kinetic advantage for catalysis within a few Angstroms of the photoelectrode surface.

Interfacial electron transfer kinetic measurements were undertaken to test the theoretical prediction that an increase in quantum mechanical mixing at the instance of electron transfer lowers the absolute value of the Gibbs free energy change. Bridge units that provided strong (adiabatic) and weak (non-adiabatic) electronic coupling, without a significant change in the geometric distance, were synthesized and anchored to semiconducting oxide surfaces for light initiated kinetic study [4,5,6]. The data supported theoretical predictions that indicated a measurable free energy loss for energy conversion schemes that employ strong electronic coupling. The implications for solar energy conversion will be discussed.

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[2] M. Kessinger, A. Soudackov, J. Schneider, R.E. Bangle, S. Hammes-Schiffer, G.J. Meyer *J. Am. Chem. Soc.* 144, 20514-20524 (2022).

[3] J. Schneider, R.E. Bangle, E.J. Piechota, G.J. Meyer *J. Am. Chem. Soc.* 142, 674-679 (2020).

[4] R.N. Sampaio, E.J. Piechota, L. Troian-Gautier, A.B. Maurer, C.P. Berlinguette, G.J. Meyer *Proc. Nat. Acad. Sci. USA* 115, 7248-7253 (2018).

[5] E.J. Piechota, R.N. Sampaio, L. Troian-Gautier, G.J. Meyer *J. Am. Chem. Soc.* 140, 7176-7186 (2018).

[6] E.J. Piechota, R.N. Sampaio, L. Troian-Gautier, A.B. Maurer, G.J. Meyer *J. Phys. Chem. C* 123, 7248-7253 (2019).