Reorganization Energy for Interfacial PCET

Scientific Achievement

Here we describe a photoelectrochemical approach for determination of the reorganization energy (λ) for proton-coupled electron transfer (PCET) reactions with application to a well-known molecular water oxidation catalyst.

Significance and Impact

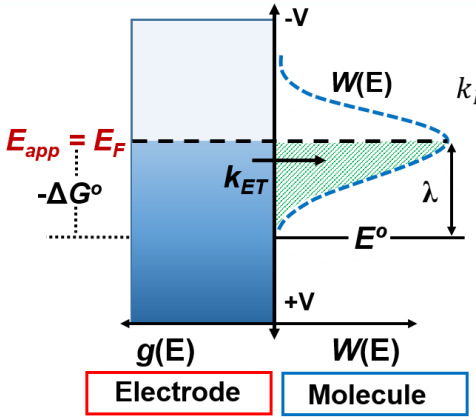
The flow of electrons *and* of protons are important for solar water splitting, yet only the former is usually quantified. The reorganization energy for PCET was found to be about twice that for electron transfer, a finding that impacts energy conversion and storage.

Research Details

- The water oxidation catalyst shown was anchored to mesoporous thin films of In_2O_3:Sn (ITO).
- Pulsed light initiated excited state injection and the subsequent recombination was quantified over an 800 mV potential range from pH 0 (ET) to 5 (PCET).
- Marcus-Gerischer analysis of the kinetic data provided values for λ_{ET} = 0.5 eV and λ_{PCET} = 0.9 eV.

Schneider, J.; Bangle, R. E.; Swords, W. B.; Troian-Gautier, L.; Meyer, G. J. *J. Am. Chem. Soc.* **2019**, *141*, 9758-9761. DOI: 10.1021/jacs.9b01296

Work was performed at UNC Chapel Hill.

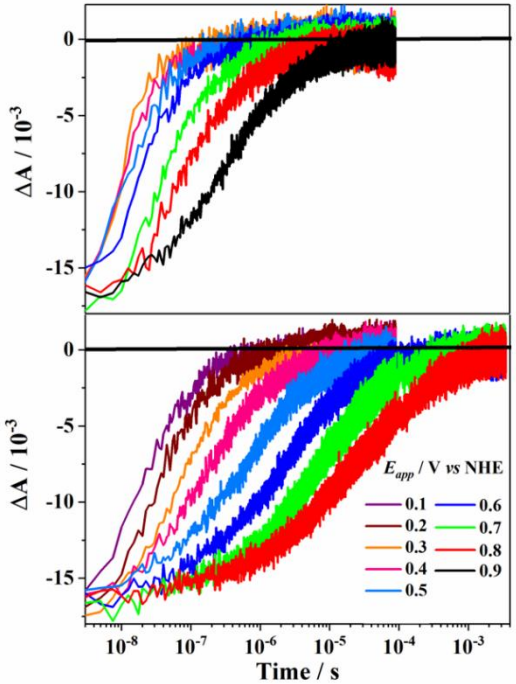


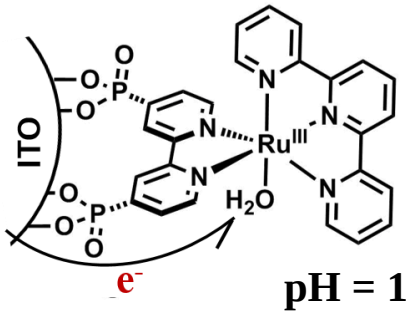
$$k_{ET} = \frac{2\pi}{\hbar} H_{DA}^2 \int_{-\infty}^{\infty} g(E) f(E, E_F) W(E) dE$$

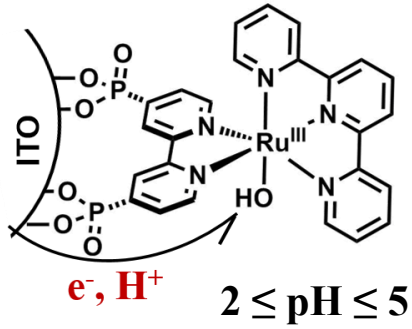
Electrode Molecule

$$W(E) \sim exp\left(\frac{-(\Delta G^\circ(E) + \lambda)^2}{4\lambda k_B T}\right)$$

$$-\Delta G^o = E^o - E_F$$







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