Electron Transfer and Proton-Coupled Electron Transfer Kinetics and Reorganization Energies at a Conductive Metal Oxide Interface

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Background

In light of the current climate crisis exacerbated by the burning of fossil fuels for energy (top right), alternative fuel sources are needed to meet current and future energy demands. Solar power has long been considered a viable alternative energy source, as the amount of sunlight that strikes the earth continuously is orders of magnitude greater than global energy consumption.

Currently, solar energy is primarily used to generate electricity either directly via photovoltaic cells or indirectly through heating water to drive conventional steam turbines. However, the energy output of these methods varies significantly over the course of the day as the intensity of incident sunlight changes. Peak solar hours, the term for the time of day with the most direct sunlight, occur just past midday and do not align with peak energy demand, which occurs in the mornings and evenings.
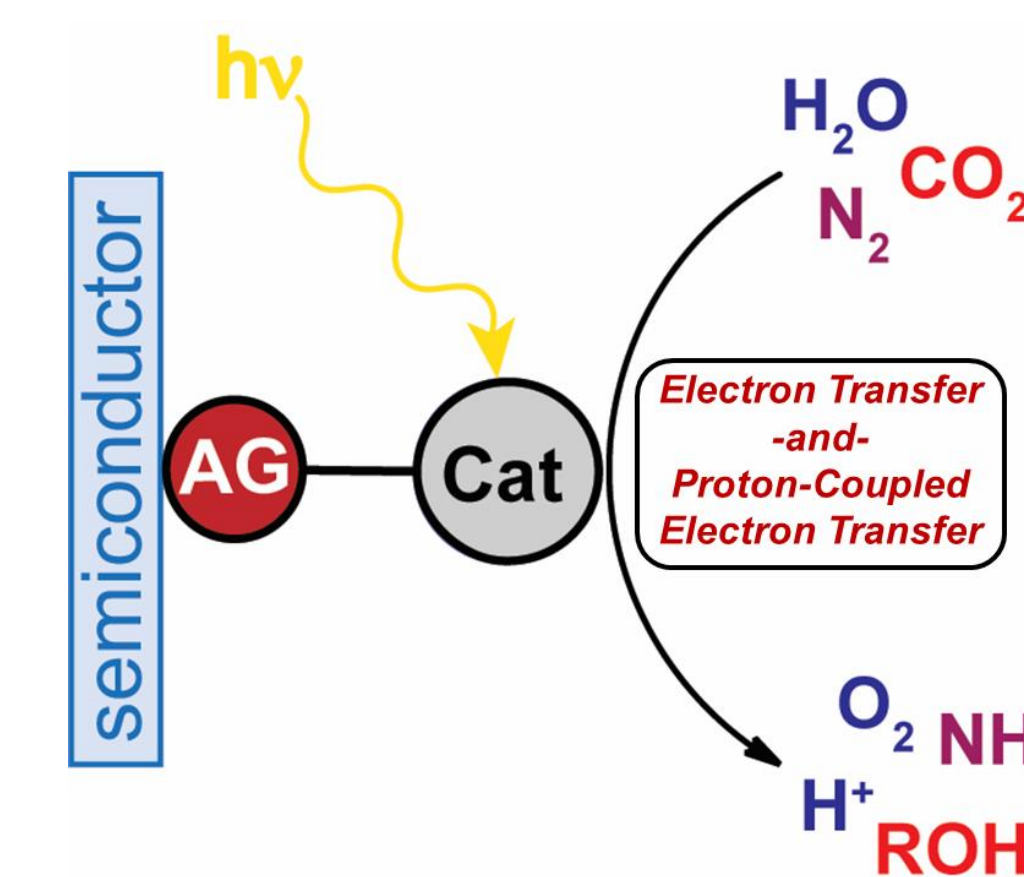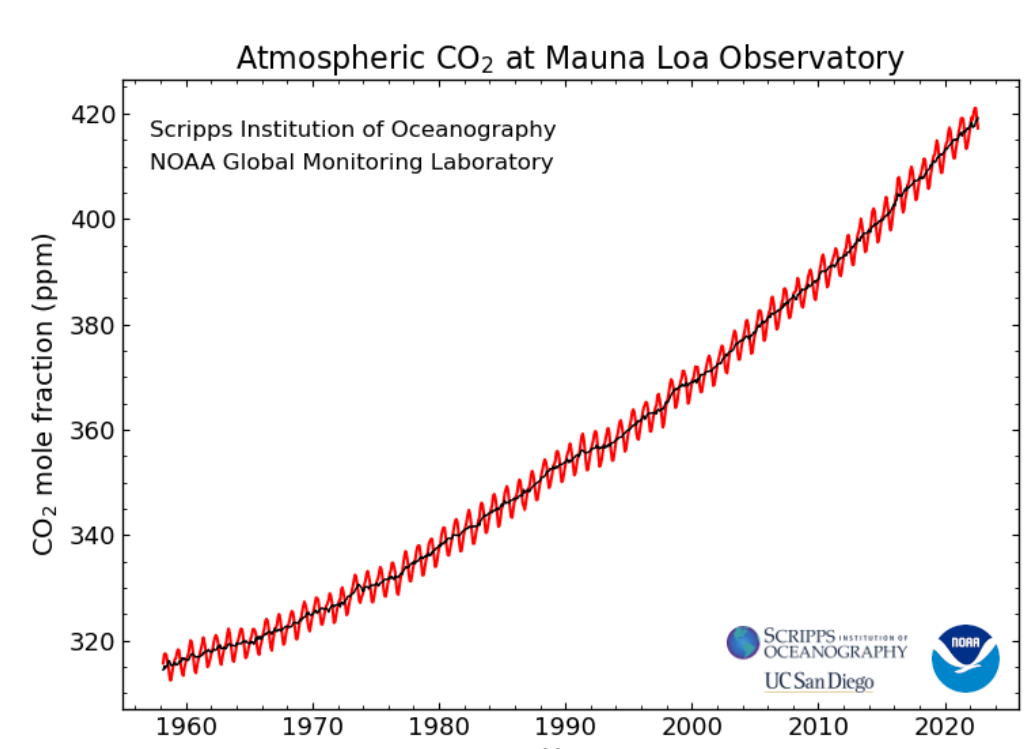

Without the means to store the generated solar energy, these methods remain impractical and require supplemental energy from traditional sources. Instead, in a process known as artificial photosynthesis, sunlight can be harnessed in the production of fuels from abundant starting materials via water oxidation, which allows for the storage of solar energy in stable chemical bonds as part of usable fuels (above).
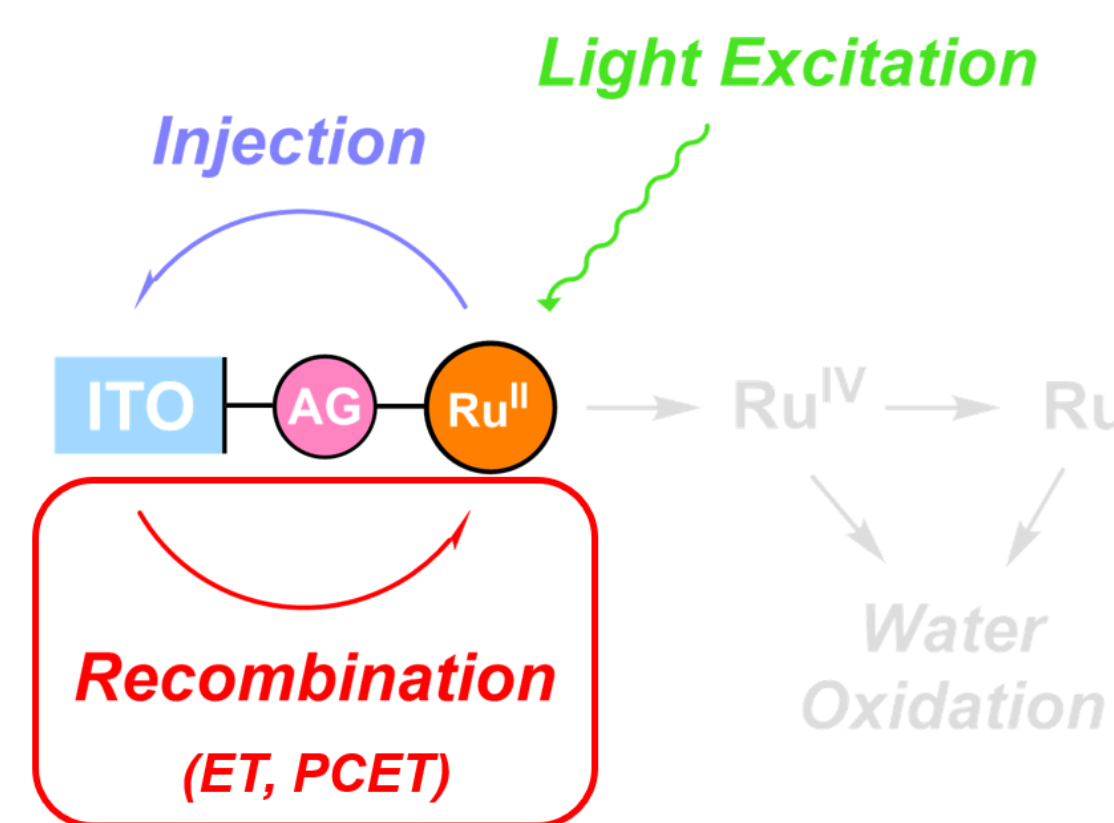
This strategy integrates a model molecular catalyst, Ru(tpy)(bpy)OH₂, or 2,2':6',2''-terpyridine-2,2'-bipyridine ruthenium (II) aquo, with a conductive metal oxide substrate (In₂O₃:Sn, ITO). When attached to ITO and excited with visible light, an electron is promoted to its excited state and rapidly transferred to the ITO substrate. This generates a freely separated electron inside the ITO and a Ru(III) metal center. This Ru(III) species can be further oxidized to Ru(IV) and Ru(V), which then are able to effectively perform water oxidation. However, the separated electron can also recombine with the Ru(III) metal center, reducing it to Ru(II) and interfering with the photocatalytic process (above). This process can occur through electron transfer (ET) or proton-coupled electron transfer (PCET) (below, right).

Since water oxidation presents a kinetic bottleneck to artificial photosynthetic schemes, understanding the kinetics of charge recombination and how experimental parameters such as the solution pH influence this unwanted reaction provides valuable insight into the optimization of water oxidation strategies. Herein, Herein, we study the ET and PCET reaction kinetics of the parasitic back electron transfer using Ru(tpy)(bpy)OH₂.
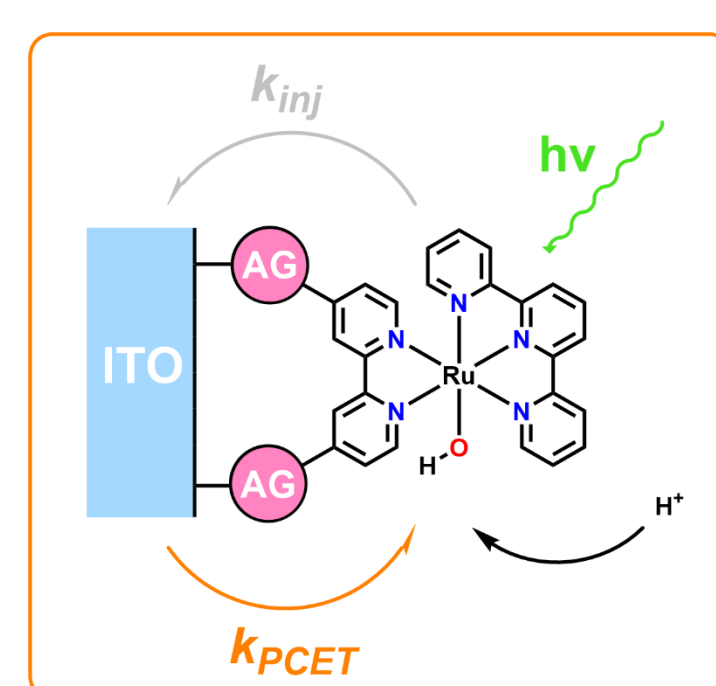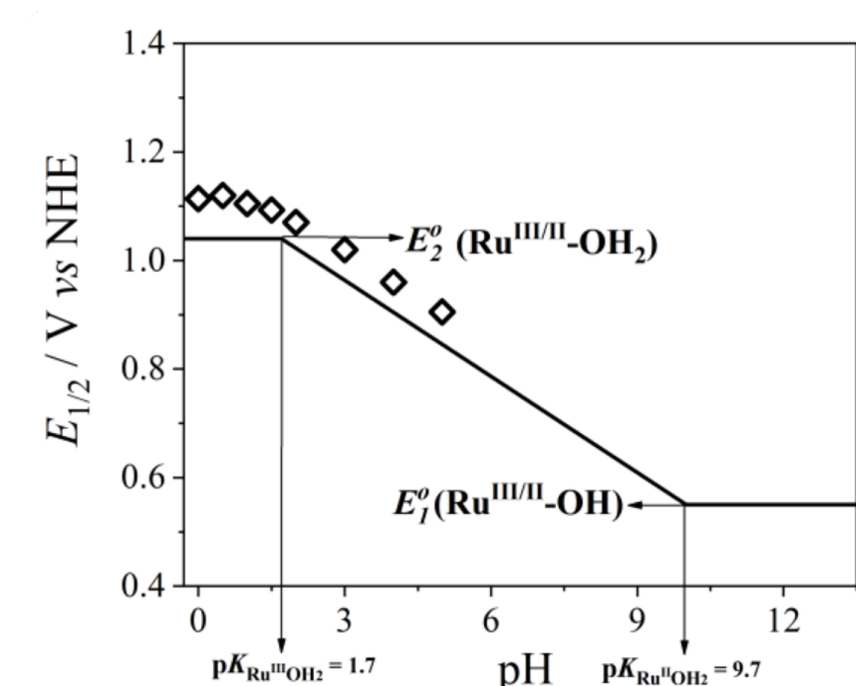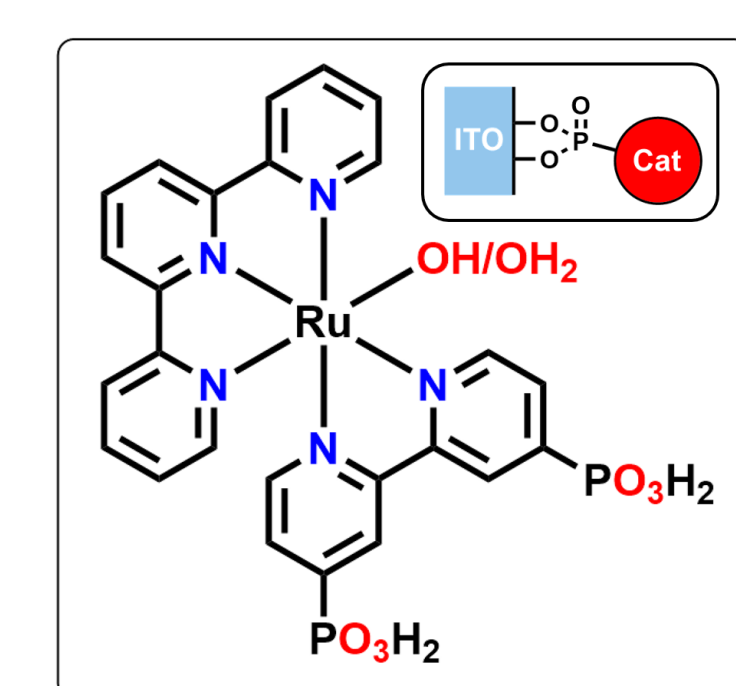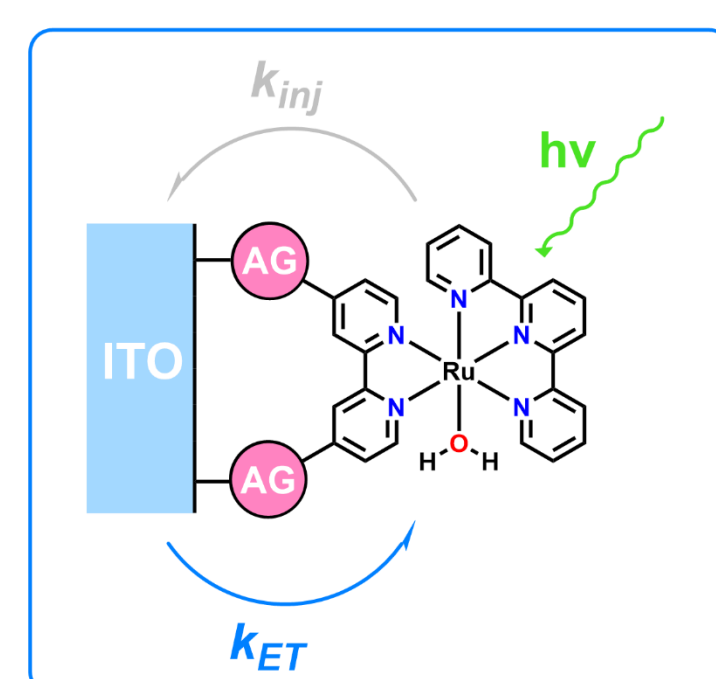
Previous work in the Meyer lab has reported on the electrochemical behavior of the model water oxidation catalyst used here in solution as well as anchored onto a transparent conductive oxide electrode with the aid of a phosphonate-based anchoring group (above, left). These early studies demonstrated that the kinetics of the associated recombination reaction were significantly slower when a PCET mechanism was operative over a purely ET reaction mechanism.[1] However, a clear limitation of these studies was that phosphonate anchoring groups do not tolerate alkaline conditions and the catalyst experienced significant desorption from the electrode above pH 5 (above, center). As water oxidation is more facile under basic or neutral conditions when compared to acidic conditions, the inability of the anchoring group to withstand pH > 5 was problematic. A more robust anchoring method was needed in order to gain a more complete understanding.

Methods
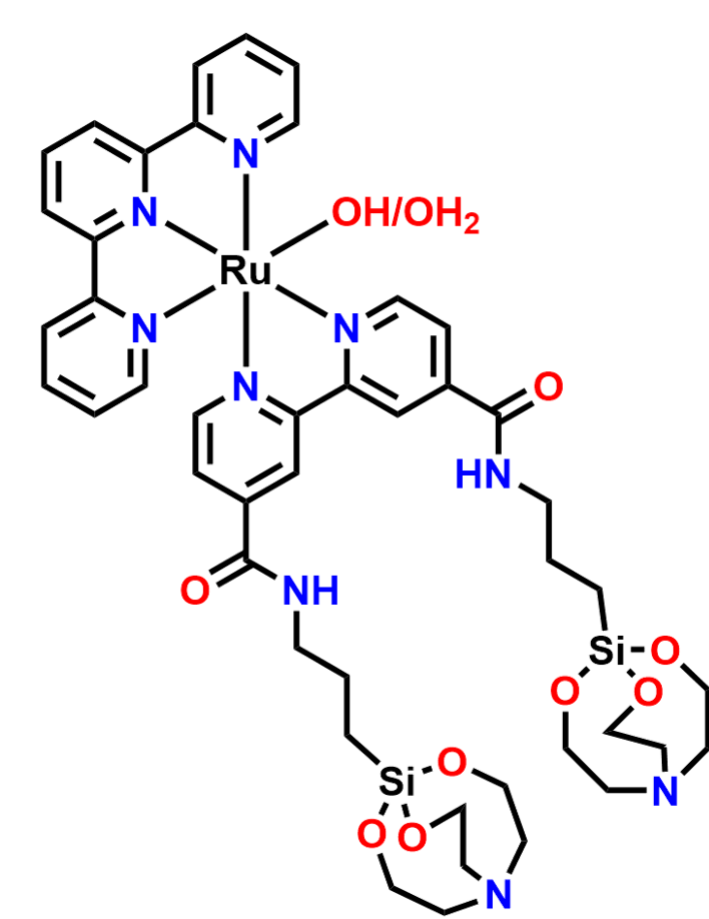
Ru(tpy)(bpy-Sil)OH₂, where bpy-Sil is 4,4'-diamidopropylsilatrane-2,2'-bipyridine, was synthesized and anchored on a degenerately-doped ITO thin film deposited on a fluorine-doped tin oxide (FTO) glass substrate (left). When anchored, the catalyst is attached to the metal oxide via siloxane bonds, while in solution, the anchoring group is protected with a triethylamine cage. Ideally, the siloxane attachment should prove hardier than the phosphonate group, as the formation of direct Si-O-MO$_x$ bonds are more resistant to alkaline conditions than dative P-O--MO$_x$ bonds.[2,3] The electron transfer and proton-coupled reactions were experimentally probed using transient pump probe spectroscopy, and the kinetics were analyzed through the lens of Marcus-Gerischer theory.

Marcus-Gerischer Theory

Marcus-Gerischer theory provides a theoretical framework for the rates of electron transfer reactions at an interface involving a molecular catalyst and a conductive metal oxide substrate (right). For this project, we focus on two parameters. The reorganization energy, λ, represents the energy input required to rearrange the reactant such that the appropriate geometry is achieved for an electron transfer reaction and provides valuable insight into the tuning of reaction kinetics. The maximum rate constant, k_{max}, provides a direct quantification of the reaction kinetics. [4-8]
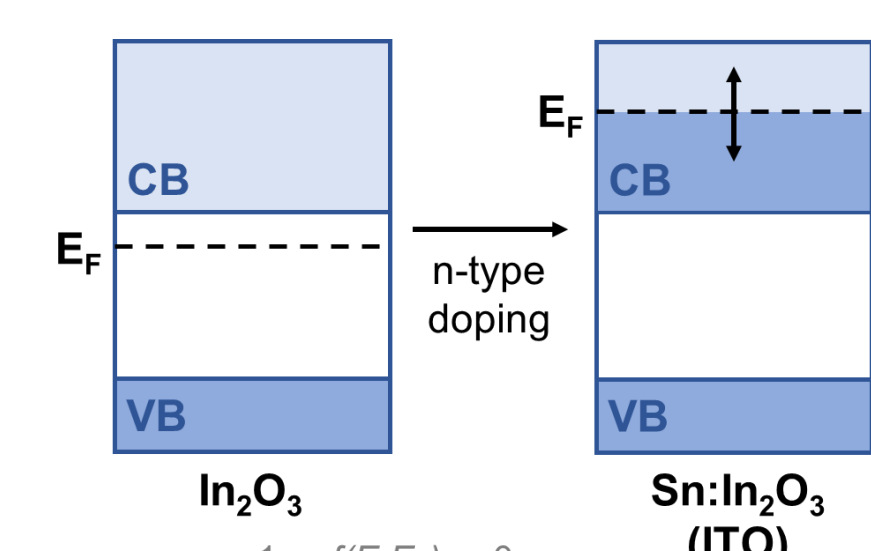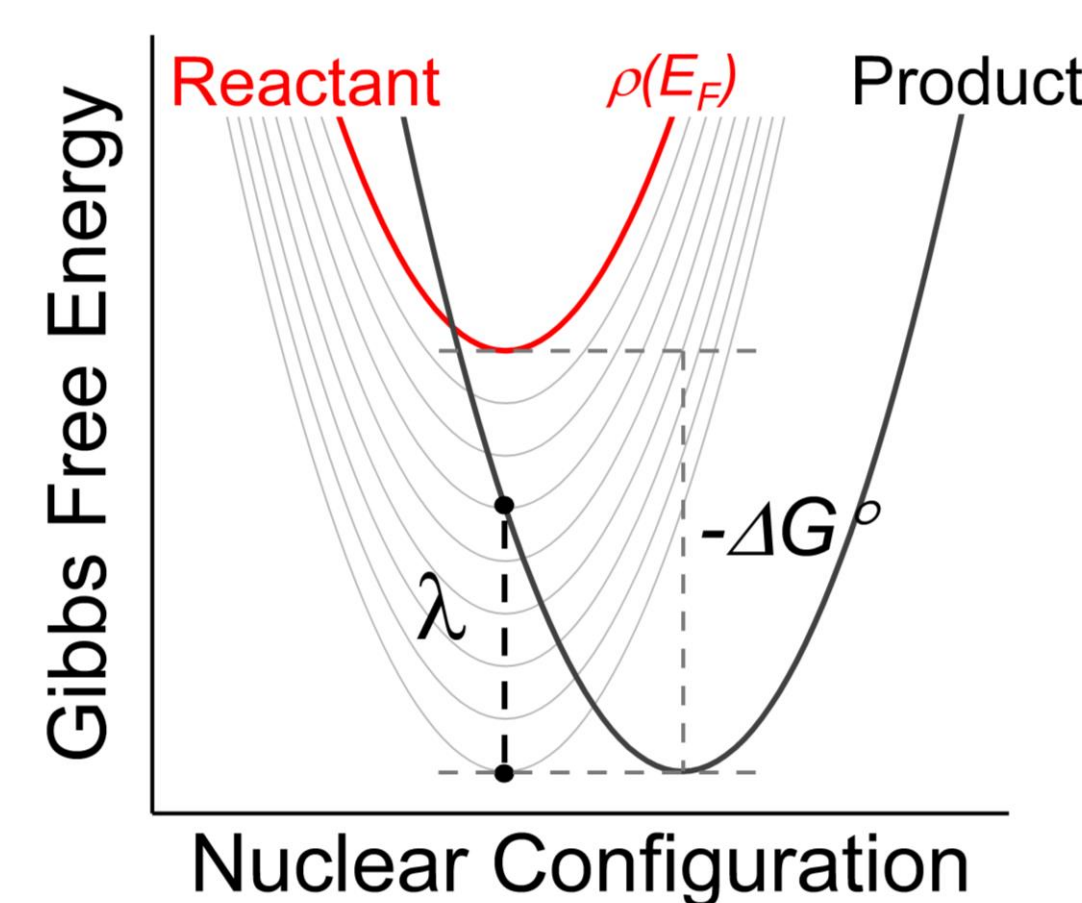

In a degenerately doped electrode, the Fermi level E_F is moved into the conduction band and can be shifted by varying an applied potential (left, top). In this case, the donor is represented by $\rho(E)$, a distribution of electronic states in the conduction band of the metal oxide, with their occupancy determined by the Fermi-Dirac distribution $f(E, E_F)$. There is a continuum of filled states below E_F that will readily transfer an electron to the acceptor, each with an associated $\Delta G^{\ddagger}$ (above). [4-8]

The shaded region on the left shows the available filled electronic states of the electrode poised to participate in interfacial electron transfer, while the green Gaussian curve is the function $W(E)$ and represents the distribution of energy barriers for the molecular catalyst. The horizontal arrows represent electron transfer processes from the metal oxide to the catalyst. [4-8]

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

$$W(E) = \frac{1}{\sqrt{4\pi k_B T}} \exp\left(\frac{-(\Delta G^\circ + \lambda)^2}{4\lambda k_B T}\right)$$

As the driving force increases, the reaction rate increases until the filled states of the electrode are sufficient in energy to completely overcome the distribution of energy barriers for electron transfer to the acceptor, whereupon the rate constant reaches a maximum k_{max}. The figure below shows the saturation of the acceptor energy barrier distribution as the filled electrode states are raised higher in energy. We can observe that the rate increases initially, but plateaus once the distribution of kinetic barriers to the acceptor is completely overcome. The reorganization energy can be then extracted mathematically. [4-8]
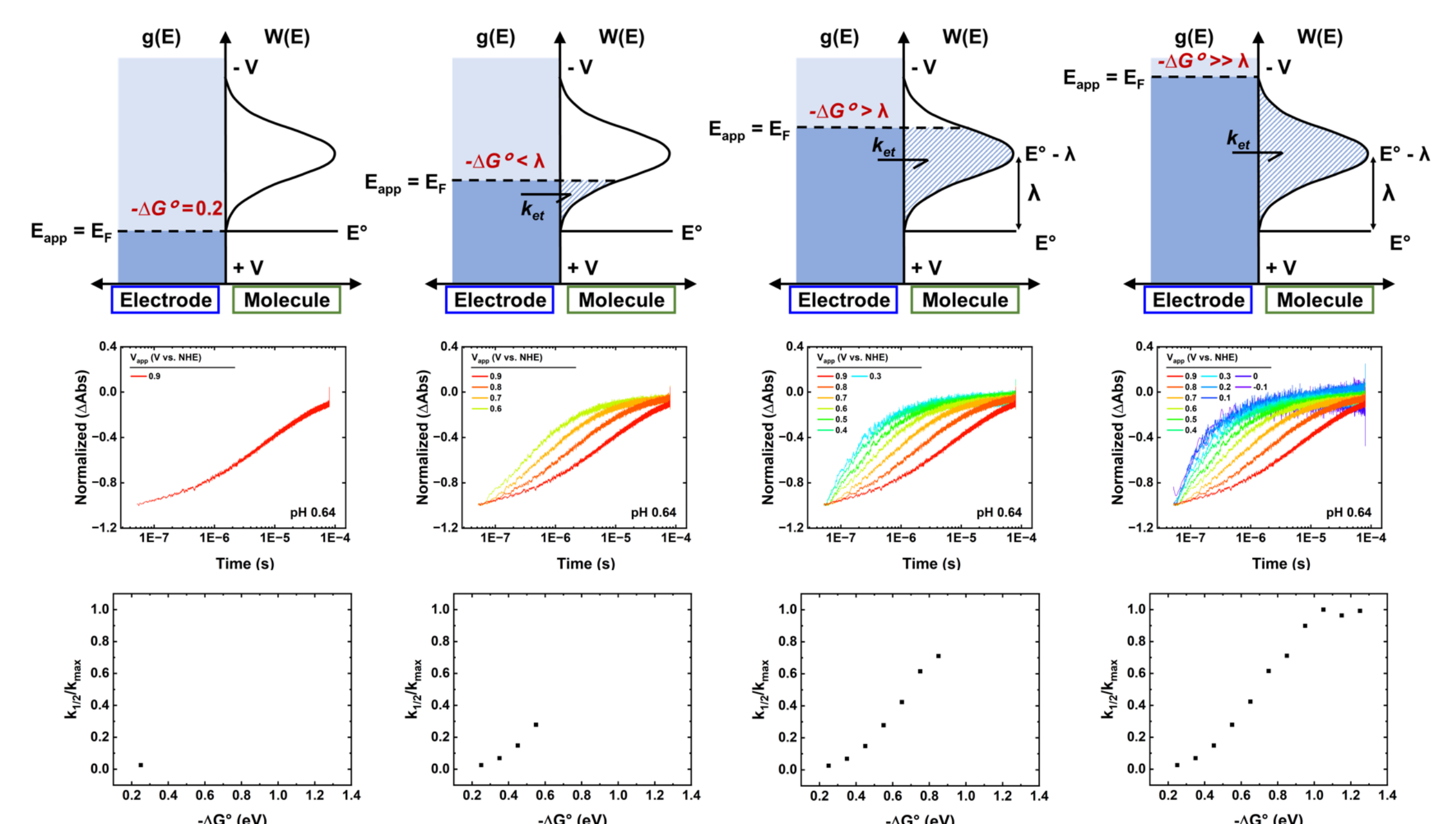

Results
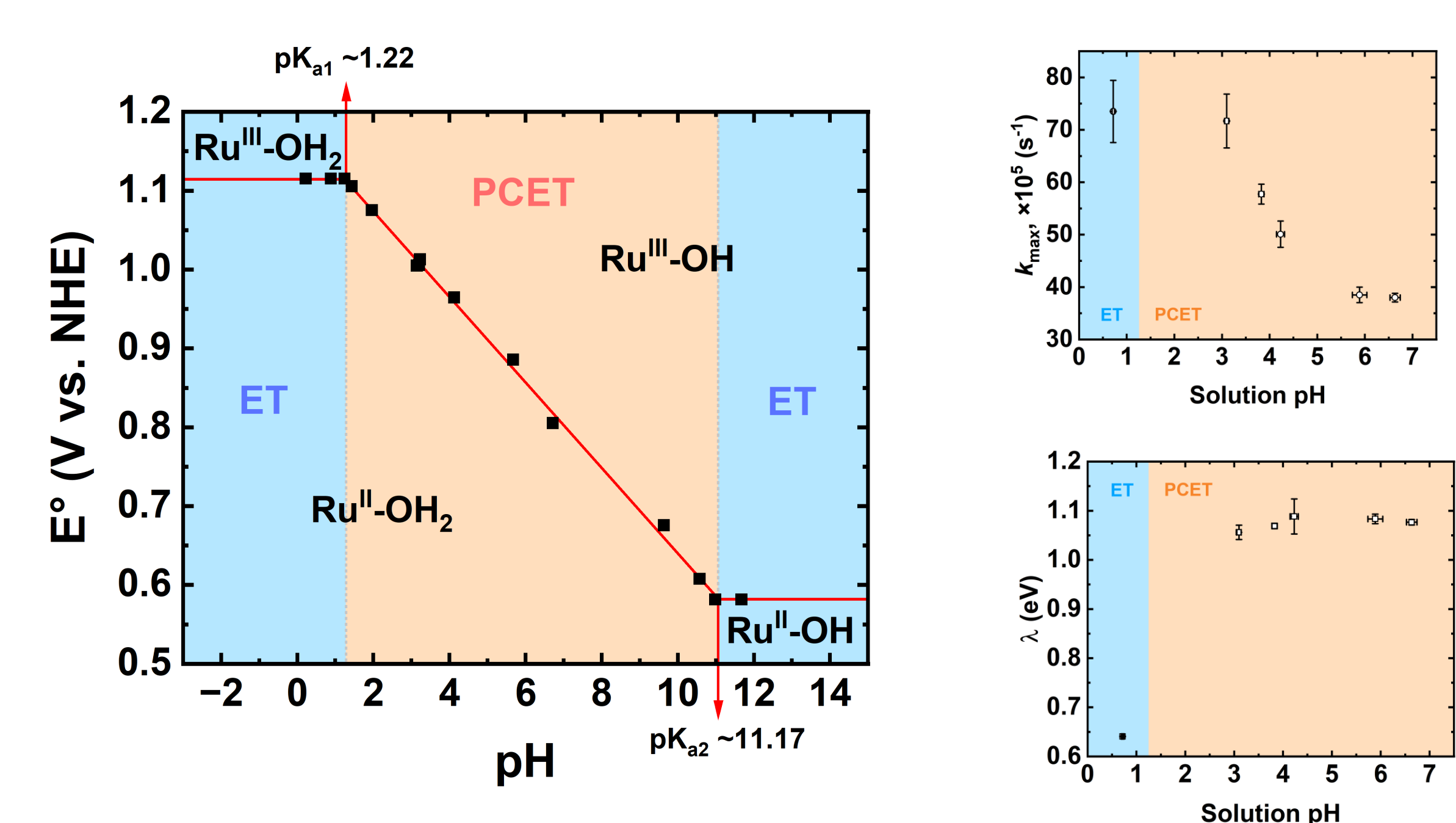
Spectroelectrochemical methods were used to construct a more complete Pourbaix diagram with the anchored catalyst (above, left). The Pourbaix diagram collected on ITO reported a slope of -53.6 mV/pH, suggesting a one electron, one proton process. The stark difference between the reorganization energies associated with electron transfer and proton-coupled electron transfer reactions are indicative of an additional kinetic barrier faced by the PCET mechanism. The additional energetic input required for PCET reactions is indicated by the larger magnitude of ΔG° required to reach k_{max} when compared to the ET data collected at pH 0.72 (below). Furthermore, we can observe the slowdown of the reaction kinetics as a result of the added energetic requirements for PCET over ET. Figure 5.7 shows the consequent decline in k_{max} as the solution pH increased and approached neutral.

Table 1. Reorganization energies and maximum rate constants for the back electron transfer and proton-coupled electron transfer reactions from ITO to Ru(tpy)(bpy-Sil)OH₂.

Solution pH	λ (eV)	k_{max} x 10⁻⁵ (s⁻¹)
0.72 ± 0.02	0.641 ± 0.001	73.5 ± 5.9
3.10 ± 0.04	1.056 ± 0.015	71.6 ± 5.1
3.83 ± 0.06	1.069 ± 0.006	57.7 ± 1.9
4.23 ± 0.08	1.088 ± 0.034	50.1 ± 2.5
5.89 ± 0.15	1.083 ± 0.010	38.5 ± 1.5
6.63 ± 0.11	1.077 ± 0.006	38.0 ± 0.8

Based on these results, water oxidation is significantly more facile at higher pH values, where recombination proceeds through slower proton-coupled electron transfers. The results and techniques from this project may be applied in the design of more optimized photocatalytic systems that further slow or block back electron transfer altogether under alkaline conditions.
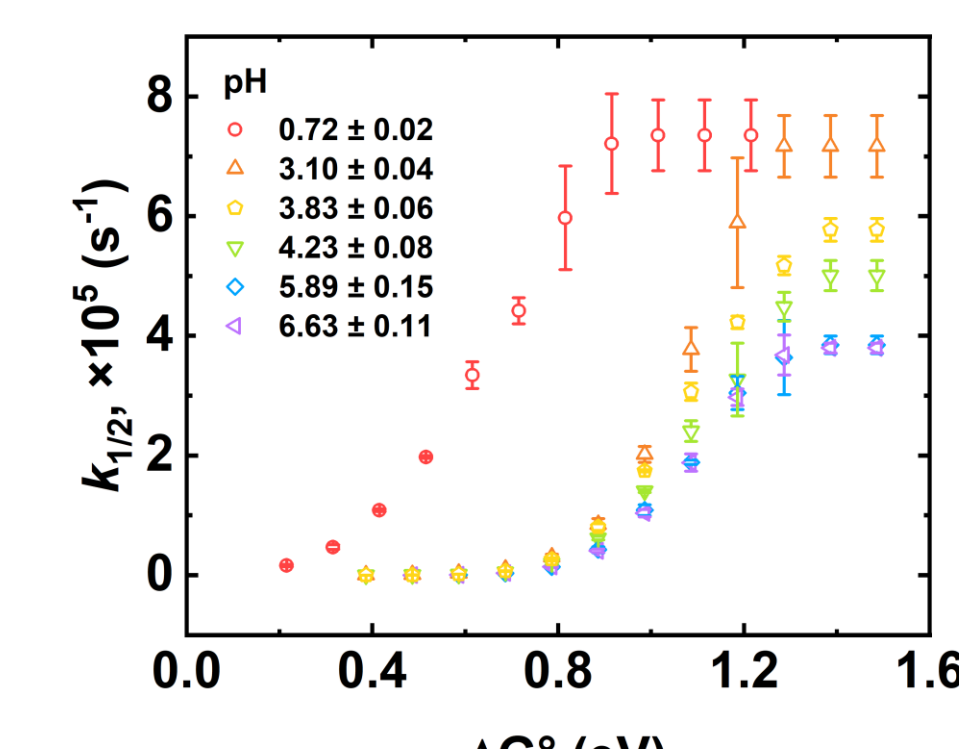
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