

PHYSICAL CHEMISTRY SEMINAR



Prof. Franz Geiger

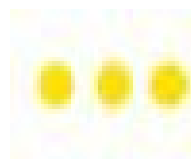
Department of Chemistry
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Monday, November 6, 2023

4:00 PM | YH 4222

Mani L. Bhaumik Collaboratory -
 Dongwon Yoo Seminar & Conference Hall

Photonic Electrochemistry



Abstract: Water's oxygen is the electron source in the industrially important oxygen evolution reaction, but how water interacts with an electrode remains enigmatic. While much microscopic insight into the Stern layer comes from atomistic simulations or joint theory-experiment approaches, water's strong absorber problem has clouded our view of how water aligns in response to applied potentials. Here, we employ nonlinear optics with a non-resonant pulse triplet at Ni:NiOx electrodes during cyclic voltammetry at pH 13 to quantify $\mathcal{N}_{\text{water}\downarrow}$, the Stern layer water molecules pointing their oxygen atoms towards the electrode, and F_{tot} , the total interfacial potential. $\mathcal{N}_{\text{water}\downarrow}$ varies sigmoidally with applied potential, U , but linearly with F_{tot} . While there is no net alignment at $U=0.4$ V, 3/4 of a water monolayer align at $U=0.6$ V and E_{flip} , the energy associated with water flipping, matches liquid water's cohesive energy. At $U=0.8$ V, all Stern layer water molecules ($1 \times 10^{15} \text{ cm}^{-2}$) align and E_{flip} matches the cohesive energy of ice. The current density is exponentially sensitive to $\mathcal{N}_{\text{water}\downarrow}$ and E_{flip} . Our experiments provide new benchmarks for electrical double layer models and a diagnostic tool for molecular electrochemistry.