

MEASURING ELECTRIC FIELDS AND INTERFACIAL SOLVATION AT ELECTROCHEMICAL INTERFACES USING SUM FREQUENCY GENERATION VIBRATIONAL SPECTROSCOPY

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This talk will describe the application of sum frequency generation (SFG) vibrational spectroscopy to understand the relationship between interfacial charge transfer, solvation structure, and surface reactivity at electrode/electrolyte interfaces. Observing interfacial solvation structure under conditions relevant for electrocatalysis represents a major challenge for bridging surface science and electrochemistry. Employing plasmon-enhanced SFG, it is possible to detect the very low steady state surface coverage of CO produced on gold during electrochemical reduction of CO₂ and to use this as a Stark reporter of interfacial solvation structure. Because CO₂ reduction is extremely sensitive to catalyst surface structure, it is necessary to differentiate between CO adsorbed to inactive (i.e., spectator) sites compared to CO produced directly at active surface sites. Separating signals from these species, we show that electrolyte cations retain their entire solvation shell upon adsorption to inactive sites, while active sites retain only a single water layer between the gold surface and the adsorbed cation. We also measure the total interfacial electric field as a function of electrolyte cation and show that this field can be separated into two independent contributions from the electrochemical double layer (Stern field) and from the polar solvation environment (Onsager field). Although both contributions to the electric field depend strongly on the identity of the alkali cation, correlating SFG spectra with reaction kinetics reveals that it is actually the solvation-mediated Onsager field that governs the cation-specific chemical reactivity at the electrode/electrolyte interface. These findings highlight the importance of understanding and controlling interfacial solvation in electrochemical systems, a challenge that will require ongoing collaboration between experiment and theory.