Many electrocatalytic reactions of current interest involve the transfer of multiple protons and electrons. Examples include the oxidations of methane and small organic molecules, as well as the reductions of nitrogen, nitrate, and carbon dioxide. These processes exhibit poor selectivity for specific desired products. This poor product selectivity hinders the adoption of these promising technologies. The aqueous electrochemical reduction of carbon dioxide to hydrocarbons on Cu electrodes is prototypical for this class of processes. It could potentially provide sustainable pathways to renewable fuels and valuable commodity chemicals, such as ethylene. Improving the selectivity for ethylene, the commodity chemical with the highest yearly production volume, is one of the most critical challenges in carbon dioxide reduction. The reaction selectivity is determined by the electrocatalytic interface, whose properties are jointly determined by the solid electrode and the liquid electrolyte. Often, these properties evolve under operating conditions. To design catalytic interfaces with high selectivity, it is essential to identify the molecular-level origins that are principally responsible for controlling the reaction path. Due to the chemical complexity and dynamic nature of the electrocatalytic interface, this molecular-level understanding is largely lacking to date. To address this challenge, we employ surface-enhanced infrared absorption spectroscopy (SEIRAS) for probing the interactions of surface-adsorbed carbon monoxide, a key reaction intermediate in the reduction of carbon dioxide to hydrocarbons, with the Cu electrode surface and the liquid reaction environment. We complement this approach with differential electrochemical mass spectrometry (DEMS) to establish interfacial property/product selectivity relationships. In this talk, we will show that an intermolecular interaction between surface-adsorbed CO and interfacial water is essential for the formation of ethylene. Disruption of this interaction shuts down the pathway to ethylene. Further, we will demonstrate that a pH- and potential-induced reconstruction of the Cu electrode drives the conversion of atop-bound CO to bridge-bonded CO. We found that only atop-bound CO is an on-pathway intermediate in CO reduction, whereas bridge-bonded CO is electrochemically inert. We will discuss how these findings contribute to the mechanistic understanding of carbon dioxide reduction and how they inform the design of more selective electrocatalytic interfaces.