Hot electrons in surface chemistry: From molecular scattering to plasmonic catalysis

Nonadiabatic effects that arise from the concerted motion of electrons and atoms at comparable energy and time scales are omnipresent in thermal and light-driven chemistry at metal surfaces. Short-lived excited (hot) electrons can measurably affect molecule-metal reactions by introducing energy dissipation, dynamical steering effects, and by contributing to state-dependent reaction probabilities. [1] Furthermore, hot electrons, created by plasmonic excitation upon light exposure, can selectively activate chemical reactions at metal catalyst surfaces. We will present our recent efforts to establish molecular dynamics methods able to capture nonadiabatic and quantum effects at metal catalyst surfaces. We employ a range of methods to capture hot electron effects such as molecular dynamics with electronic friction and surface hopping dynamics. By combining linear response electronic structure calculations [2] with high-dimensional machine-learning representations, [3] we are able to perform ensemble-averaged nonadiabatic dynamics at surfaces. I will showcase this for the vibrational state-to-state scattering of NO on Au(111), [4] where we can identify the regimes in which electronic friction is valid. I will also provide a detailed analysis of the limitations of the existing approach and our ongoing efforts to include quantum tunnelling effects, memory effects, and explicit excited-state effects to capture the dynamics of light-driven hot-electron chemistry.