CHEMISTRY & BIOCHEMISTRY SEMINAR SERIES:

Kinetic Barriers to Metal Hydride Complex Formation in Fuel-forming Catalysis

Abstract:

Proton-coupled electron transfer (PCET) processes underpin the catalytic transformations that take energy-poor substrates to energy-rich fuels. Many of these catalytic transformations proceed through metal hydride intermediates. Intriguingly, mechanistic studies undertaken by our lab reveal the PCET reactions that form metal hydride intermediates almost exclusively follow a stepwise electron transfer–proton transfer pathways. Moreover, in several examples, ligands are initially protonated, followed by a tautomerization to yield the stable metal hydride product. The preference for a stepwise reaction over a concerted proton-coupled electron transfer (CPET) route that circumvents the high energy, charged intermediates associated with stepwise pathways, as well as a kinetic preference for protonating the ligand over direct metal protonation, suggests multiple factors dictate the PCET reactions that form metal hydride species. Research in our lab aims to understand the factors underpinning reaction pathways that yield metal hydride complexes.



Susannah Scott

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About the Speaker:

Jillian L. Dempsey is a professor at the University of North Carolina at Chapel Hill where she holds the Bowman and Gordon Gray Distinguished Term Professorship. She is currently the Director of the Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE) and an associate editor for ACS Electrochemistry.

Jillian received her S.B. from the Massachusetts Institute of Technology in 2005 where she worked in the laboratory of Prof. Daniel G. Nocera. As an NSF Graduate Research Fellow, she carried out research with Prof. Harry B. Gray and Dr. Jay R. Winkler at the California Institute of Technology, receiving her PhD in 2011. From 2011–2012 she was an NSF ACC Postdoctoral Fellow with Daniel R. Gamelin at the University of Washington.

In 2012, Jillian joined the faculty at the University of North Carolina at Chapel Hill. Her research group explores charge transfer processes associated with solar fuel production, including proton-coupled electron transfer reactions and electron transfer across interfaces. Her research bridges molecular and materials chemistry and relies heavily on methods of physical inorganic chemistry, including transient absorption spectroscopy and electrochemistry.

She has received numerous awards including the Harry B. Gray Award for Creative Work in Inorganic Chemistry by a Young Investigator (2019), the J. Carlyle Sitterson Award for Teaching First-Year Students (2017), a Sloan Research Fellowship (2016), a Packard Fellowship for Science and Engineering (2015), the Agnes Fay Morgan Research Award (2020), and the University Award for Advancement of Women (2021).