Potential-Dependent Reorientation of Small Molecules on Electrode Surfaces

Xiao Li and Andrew A. Gewirth
Department of Chemistry, University of Illinois,
600 S. Mathews Avenue, Urbana, IL 61801

In this talk on electrode processes, we report on our recent work utilizing a combination of electrochemical, vibrational spectroscopic, and detailed ab initio calculations to examine the potential dependent reorientation of small molecules on electrode surfaces. A particular focus is the changes undergone by the small molecule SCN- on Au. We show that this molecule is N-bound to the Au surface at negative potentials, S-bound at intermediate potentials, and bridging at positive potentials. Interestingly, while the Stark shift of the C-N stretch is normal (positive) for the S-bound form, it is negative for the bridge bound SCN. We utilize detailed calculations to explain this behavior. The calculations show that the origin of the potential-dependent reorientation derives from the overlap between specific localized orbitals on the SCN and the Fermi level of the Au surface. As the Fermi energy changes due to the change in potential, this overlap also changes, and the molecule reorients to find the lowest energy configuration. The origin of the different Stark shifts arises from the change in nature of the LUMO on the SCN in the different orientations. For S-bound SCN, the LUMO is antibonding, as normally found. However, for bridge-bound SCN, this LUMO is bonding.

Extension of this insight to other molecular systems will be discussed.