Physical Chemistry Student Seminar

"From Poison to Small-Molecule Probe: Cyanide Self-Assembly on Au{111} for the Development of Room-Temperature Single-Molecule Spectroscopy"

Cyanide self-assembles on gold providing a unique opportunity to understand the coupling between substrate electrons and molecular vibrations. Two factors, the strength of the substrate-molecule coupling and the favorable orientation of the molecular orbitals, directly influence the efficiency of electron transfer across a molecule to the substrate. Inelastic electron tunneling can probe molecule vibrations; the contributions to the tunneling current can be measured at the single-molecule level under ultrastable conditions using a scanning tunneling microscope. Molecular vibrations, most often probed using infrared or Raman spectroscopy, encode chemical information pertaining to connectivity, composition, and geometry and can be used to monitor chemical reactions and to sense changes due to the local environment. Predicted to have a vibrational resonance with the surface electronic states of gold, cyanide is an ideal small molecule to probe the interactions between electronic structure and vibrations. Exploiting well-known cyanide-gold coordination chemistry, I first characterize both the structural and vibrational properties of monolayers of cyanide on gold that are stable under ambient conditions and demonstrate that the substrate-molecule coupling of cyanide is particularly strong, leading to facile electron transfer between the molecules to the substrate. Following the characterization of the as-adsorbed cyanide system, I discuss how through a simple thermal annealing process I induce local electronic, chemical, and structural changes in the cyanide monolayer that can be identified through a blue shift of the C-N bond vibrational energy. Finally, I describe a prototype ambient scanning tunneling microscope that uses the multiplexed signal from Fourier transform infrared spectroscopy through rear illumination via attenuated total internal reflection to test whether the exponentially weighted tunneling current can detect single-molecule vibrations through an atomically sharp tip. This effort contributes to understanding the interactions between electronic structure and molecular vibrations through the use of cyanide coordination chemistry with the long-term goal of creating a generally applicable method of getting single-molecule chemical information while simultaneously acquiring, in space and time, the local environmental structure from the scanning tunneling microscope.

Presented by

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