

AFM-Raman-TERS Workshop
September 27, 2016
Northwestern University

“Nanoscale Chemical Imaging and Single Molecule Spectroscopy”

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As an introduction I will provide some background material on the basic physical concepts underlying surface-enhanced Raman spectroscopy (SERS) and tip-enhanced Raman spectroscopy (TERS). This will be followed by a discussion of two recent advances in ultrahigh vacuum (UHV) TERS which illustrate the power of this vibrational nanoscopy. Finally, I will discuss our recent efforts to probe electrochemical reactions at the nanoscale using electrochemical (EC) TERS.

In the area of ultrahigh vacuum TERS (UHV-TERS), we will first discuss our current understanding of the adsorbate-surface and adsorbate-plasmon interactions involved with the molecule N-N'-bis(2,6-diisopropylphenyl)-perylene-3,4:9,10-bis(dicarboximide) (PDI) on various single crystal surfaces (viz., Ag(111), Ag(100), Cu(111), and Au(111)) which are probed by a Ag TERS tip. This study demonstrates that TERS has a reasonable degree of surface generality. Second, we provide some new insights into the nature of a dynamic phase boundary involved in the room temperature (RT), UHV-TERS of the Ag tip/ N-N'-bis(2,6-diisopropylphenyl)-1,7-(4'-t-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) (PPDI)/Ag(100) system. The orientation of PPDI molecules at the dynamic molecular domain boundary has been unravelled with ~4 nm spatial resolution by UHV-TERS mapping. This last topic demonstrates that TERS provides access to molecular adsorption geometries in regions with no STM topographical information.

In the area of electrochemical TERS (EC-TERS), we will discuss the nanoscale redox behavior of the molecule Nile Blue (NB), and compare these results with conventional cyclic voltammetry (CV). We successfully monitor the disappearance of the 591 cm^{-1} band of NB upon reduction and its reversible reappearance upon oxidation during the CV. At ~0.01 ML coverage we observe step-like behavior in some TERS voltammograms corresponding to reduction and oxidation of single or few NB molecules. Further, we also show that the coverage of NB is nonuniform across the ITO surface. We conclude with a discussion of the general considerations for using TERS to study single molecule electrochemical processes.