Electromagnetic Field Enhancement near 50nm Ag Nanocrystals, and the Raman Spectra of Single Molecules

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Surface Enhanced Raman Spectroscopy (SERS) is an old subject; yet the mechanism and strength of the phenomenon remain uncertain. We find that Individual chemisorbed R6G dye molecules are detected with an effective Raman cross section of about 200 square Angstroms, on individual compact aggregates of 30-50 nm Ag crystallites. The apparatus incorporates dark- field optical microscopy for Resonant Rayleigh Mie scattering, in-situ AFM for topology, and wide field Raman imaging on a CCD camera. The rare, large cross section SERS sites are at the junctions between crystallites. The theory, including classical electromagnetic field enhancement and related ballistic electron propagation in the metal, will be discussed at length. Chemisorption appears essential for such a large cross section.