Understanding SERS and TERS using metal cluster models and electronic structure theory

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In this talk I describe recent studies aimed at describing plasmonics and SERS using electronic structure methods,including INDO/S and TDDFT methods.[1] Silver clusters with 10-300 atoms show plasmonic excitations that are remarkably similar to those for much larger (10-20 nm) nanoparticles, which means that one can use clusters to model processes that are usually measured for nanoparticles, especially SERS and TERS intensities that include for both electromagnetic and chemical effects, and the dependence of the SERS and TERS on potential bias. The talk will describe our latest progress with developing this theory, including studies of the chemical effect in SERS which provide new insights concerning why the static TDDFT Raman spectrum for a cluster model works well (but by accident). I also demonstrate the role of charge transfer excited states in determining the bias dependence of TERS intensities. These results will be used to interpret experiments in the Van Duyne and Apkarian labs. Finally, I consider recent measurements of enhanced Raman spectra on organic semiconductors.[2]

[1] Gieseking RL, Ratner MA, Schatz GC, *Far. Disc.* 2017, **205**, 149 – 171.

[2] Yilmaz M, Babur E, Ozdemir M, Gieseking RL, Dede Y, Tamer U, Schatz GC, Facchetti A, Usta H, Demirel G, *Nature Materials*, 2017, **16**, 918-925.