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First-principles studies of surface-enhanced Raman scattering: Benzene thiol on Au[1] ALEXEY ZAYAK, Department of Electrical Engineering and Computer Science, UC-Berkeley, CA, JEFFREY NEATON, Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA — First-principles calculations based on density functional theory are used to investigate how chemisorption of organic molecules on metal surfaces affects their Raman spectra. Experiments have long reported Raman intensity enhancements of many orders of magnitude for molecules on rough metal surfaces or near nanofabricated metallic tips. The goal of this work is to explore "chemical" effects that may contribute to this enhancement, specifically hybridization and charge transfer between the molecule and its metallic substrate. We consider benzene thiol chemisorbed on extended Au(111) surfaces and finite Au and Ag clusters. Using a finite-difference scheme, we compute the absorption site, molecular orientation, and coverage dependence of Raman-active phonon modes and their intensities. We also examine how the electronic structure of the molecule is modified in each case, and discuss implications for the strength of Raman processes.

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