

Abstract Submitted  
for the MAR12 Meeting of  
The American Physical Society

**First-Principles Approach to Chemical Raman Enhancement of Organic Adsorbates on Metal Surfaces**<sup>1</sup> ALEXEY ZAYAK, Molecular Foundry, LBNL, HYUCK CHOO, California Institute of Technology, YING S. HU, Rice University, DANIEL GARGAS, STEFANO CABRINI, JEFFREY BOKOR, P. JAMES SCHUCK, JEFFREY B. NEATON, Molecular Foundry, LBNL — A first-principles density functional theory (DFT)-based approach is developed [1] to determine chemical contributions to surface-enhanced Raman spectroscopy (SERS) for molecular adsorbates on metal surfaces. While SERS applications are often directed at sensing trace amounts of chemical species, quantitative calculations of how Raman spectra of molecules are altered on chemisorption [1], coupled to experiments, can contribute significantly to our understanding of the electronic structure of the metal-adsorbate interface. For two adsorbates on Au – benzene thiol and trans-1,2-bis(4-pyridyl) ethylene (BPE) – DFT calculations of the static Raman tensor demonstrate a strong mode-dependent modification of Raman spectra by Au substrates. Raman active modes with the largest enhancements result from stronger contributions from Au to their electron-vibron coupling, as quantified through a deformation potential. Based on our calculations, we introduce a straightforward analysis to extract “chemical enhancement” from measurements, and demonstrate how SERS spectra of BPE change as a function of the relative fraction of BPE molecules chemisorbed to the substrate.

[1] Zayak et al, Phys. Rev. Lett. 106, 083003 (2011)

<sup>1</sup>We acknowledge DOE for support, and NERSC for computational resources.

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Date submitted: 07 Dec 2011

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