First-Principles Studies of Chemical Raman Enhancement for Organic Adsorbates at Metal Surfaces

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Using a first-principles-based finite-difference approach based on density functional theory, we investigate how off-resonant Raman spectra of the well-studied organic molecule, benzene thiol (BT), is affected by chemisorption on planar Au(111) surfaces. Calculated Raman intensities of BT for adatom, bridge, and hollow binding sites on Au show enhancements relative to gas-phase that are both mode and binding site dependent. Predicted enhancements range from nearly zero to more than two orders of magnitude. Comparing our results with a simple model, we connect this enhancement to interfacial contributions to electron-phonon coupling and induced charge rearrangement at the metal-molecule interface. Enhancement of modes, which are both Raman and IR active, is quenched due to their electrostatic nature. Experimentally measured relative enhancements for BT adsorbed to rough Au(111) surfaces are in excellent agreement with calculations and provide compelling evidence for a strong affinity of BT for bridge sites on rough Au surfaces.