Density functional theory investigation of benzenethiol adsorption on Au(111)

We have studied the adsorption of benzenethiol molecules on the Au(111) surface by using first principles total energy calculations. A single thiolate molecule is adsorbed at the bridge site slightly shifted toward the fcc-hollow site, and is tilted by 61 degrees from the surface normal. As for the self-assembled monolayer (SAM) structures, the (2sqrt3xsqrt3)R30 degrees herringbone structure is stabilized against the (sqrt3xsqrt3)R30 degrees structure by large steric relaxation. In the most stable (2sqrt3xsqrt3)R30 degrees SAM structure, the molecule is adsorbed at the bridge site with the tilting angle of 21 degrees, which is much smaller compared with the single molecule adsorption. The van der Waals interaction plays an important role in forming the SAM structure. The adsorption of benzenethiolates induces the repulsive interaction between surface Au atoms, which facilitates the formation of surface Au vacancy. (C) 2004 American Institute of Physics.