160g Development of Classical Force Field for the Chemical Bonding between Benzenedithiolate and Gold

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We have constructed a group of classical potentials based on ab initio density functional theory (DFT) calculations to describe the chemical bonding between benzenedithiolate (BDT) molecule and gold atoms, including bond stretching, bond angle bending and dihedral angle torsion involved at the interface between the molecule and gold clusters. Three DFT functionals, LDA, PBE0 and X3LYP, have been implemented to calculate single point energies (SPE) for a large number of molecular configurations of BDT-1, 2 Au complexes. The three DFT methods yield similar bonding curves. The variations of atomic charges from Mulliken population analysis within the molecule/metal complex versus different molecular configurations have been investigated in detail. We found that, except for bonded atoms in BDT-1, 2 Au complexes, the Mulliken partial charges of other atoms in BDT are quite stable, which significantly reduce the uncertainty in partial charge selections in classical molecular simulations. Molecular dynamics (MD) simulations are performed to investigate the structure of BDT self-assembled monolayer (SAM) and the adsorption geometry of S adatoms on Au (111) surface. We found that the bond stretching potential is the most dominant part in chemical bonding. Whereas the local bonding geometry of BDT molecular configuration may depend on the DFT functional used, the global packing structure of BDT SAM is quite independent of DFT functional, even though the uncertainty of some force-field parameters for chemical bonding can be as large as ~100%. This indicated that the intermolecular interactions play a dominant role in determining the BDT SAMs global packing structure.