

I. INTRODUCTION

Self-assembled monolayers (SAMs) have attracted considerable attention as model systems for many fundamental and technological investigations¹. The thiol and thiolate-based SAMs have broad applications on supramolecular assembly, wetting, tribology, corrosion inhibition, lithography, chemical and biochemical sensors, optics, and immobilization of DNA, because of both their simplicity and stability. In particular, SAMs can simulate a biological membrane which allows adsorption of proteins to metal surfaces without denaturation²⁻⁴. The peptide molecules with some enzymatic activity can be deposited on metal surfaces via the thiol or thiolate linkage monolayer^{5,6}. The deposition of a second monolayer on the top of the first adsorbed thiol or thiolate monolayer yields a bilayer system consisting of two monomolecular films. In other words, a layer of peptide molecules can be bonded to the gold surface via the linkage monolayer formed from the thioglycolic acid (HSCH_2COOH)⁵⁻⁷.

The chemisorption of the thioglycolic acid on the gold surface was demonstrated using surface-enhanced Raman scattering⁸ and ultrafast electron crystallography⁹. It was found when the higher portion of the carboxylic acid groups is deprotonated, the higher portion of the thioglycolic acid molecules adopts a trans conformation⁸. It was also observed that after 2,2'-dithiodiacetic acid is deposited on the Au(111), the SCH_2COOH molecules are randomly oriented on the gold surface⁹, that is, the adsorption pattern related to the SCH_2COOH is different from that corresponding to the HSCH_2COOH . On the other hand, the switchable SAM under the influence of an electrical potential was observed with intentionally created room for conformational changes of the molecules¹⁰. When the external electrical potential is turned on, the hexadecanoic acid molecules ($\text{HS}(\text{CH}_2)_{15}\text{COO}^-$) bend their negatively charged COO^- group towards to the positively charged gold surface¹⁰. Simulating this switchable SAM process via the *ab initio* method requires a prohibitive amount of computer time, so one has to study the simple case: the $\text{HSCH}_2\text{COO}^-$ on the Au(111) surface.

It was recently observed that thiol stays intact when deposited on the regular Au(111) surface, but the S-H bond of the thiol is broken on the defected Au(111) surface^{11,12}. Upon the HSCH_2COOH molecules deposit on the Au(111), they can either remain intact, or turn into one of the following substances: 1) SCH_2COOH in the presence of the defect on the Au(111)^{11,12}; 2) $\text{HSCH}_2\text{COO}^-$ by increasing pH value⁸; 3) SCH_2COO^- by the defect and increasing pH value. To get a consistent picture of the thioglycolic acid adsorption on the