

# Molecular simulation study of the $c(4\times 2)$ superlattice structure of alkanethiol self-assembled monolayers on Au(111)

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We report a molecular simulation study of the  $c(4\times 2)$  superlattice structure of alkanethiols on Au(111) based on an accurate force field developed from *ab initio* quantum chemical calculations. Quantum chemical calculations were performed on both clusters and periodic systems of methylthiols on Au(111) surfaces. Molecular mechanics and dynamics simulations of alkanethiols with various chain lengths on Au(111) were carried out. The  $c(4\times 2)$  superlattice structure was predicted for various chain lengths at a wide range of temperatures using the developed all-atom force field. Simulation results further show that tilt angle decreases as temperature increases, whereas monolayer thickness increases. The accurate force field developed is useful to molecular simulation studies of various systems involving self-assembled monolayers of alkanethiols on gold surfaces. © 2002 American Institute of Physics. [DOI: 10.1063/1.1507777]

## I. INTRODUCTION

Self-assembled monolayers (SAMs) are formed by a spontaneous chemisorption of organic molecules on a substrate surface. The chemical nature of precursor molecules (e.g., head group, terminal group, and molecular chain length) determines and controls the chemical and structural properties of SAMs. The novel properties of SAMs make them ideal for applications to biomaterials, biosensors, and corrosion and wear inhibitors. A number of classes of SAM systems have been developed and characterized, including organosulfur–coinage metal, organosilicon–oxide, and carboxylic acid–metal oxide systems. Of these monolayers, alkanethiol SAMs on Au(111) surface are most commonly used as a model system for both experimental and theoretical studies.<sup>1–3</sup>

Studies of the structures of alkanethiol SAMs on Au(111) have revealed a  $(\sqrt{3}\times\sqrt{3})$  R30° lattice structure, which corresponds to a chain-chain spacing of  $\sim 5$  Å with an area of 21.6 Å<sup>2</sup> per molecular chain.<sup>3</sup> Further investigation of the structures of alkanethiol SAMs by various experimental techniques, e.g., low-energy atom diffraction (LEAD),<sup>4</sup> x-ray diffraction (GIXD),<sup>5</sup> scanning tunneling microscopy (STM),<sup>6–8</sup> and atomic microscopy (AFM)<sup>9</sup> have found a  $c(4\times 2)$  superlattice of the  $(\sqrt{3}\times\sqrt{3})$  R30° lattice. To understand the structures and properties of alkanethiol SAMs on Au(111), molecular simulations have also been carried out.<sup>10–23</sup> However, none of those molecular simulations can predict the  $c(4\times 2)$  superlattice structure, mainly due to a

lacking of an appropriate force field for alkanethiol SAMs on Au(111). For this system, the interaction between S and Au is a very important term in the force field.

To study the Au–S interaction, Sellers *et al.*<sup>24</sup> performed *ab initio* quantum chemical (QC) calculations of HS- and CH<sub>3</sub>S- on a cluster model of Au(111). They used Hartree–Fock (HF) with correlation treated at the second order of perturbation theory, and solved within a localized basis set. The Au cluster consisted of 17 atoms, of which eight were treated as quantum mechanics and others as classical objects. The adsorbed molecules (HS- or CH<sub>3</sub>S-) in the system were movable. In those clusters the thiol was kept at one three-fold *hcp* hollow site and one *atop* site. The S–Au distance calculated was 2.53 Å. In the work by Sellers *et al.*,<sup>24</sup> of the two three-fold sites (*fcc* and *hcp*), only the *hcp* was explicitly calculated. The two positions were assumed to be equivalent in energy for parameterizing the S–Au interactions in force field development. Beardmore *et al.*<sup>25</sup> used the density function theory (DFT) with the Becke gradient correction and the Lee–Yang–Parr correlation functional (BLYP) to investigate the S–Au interaction. The thiol was seated at different sites (*fcc*, *hcp*, *atop*, *bridge*, and the ones lying midway between these) onto a 17-atom Au cluster. They found that the *fcc* site was the one with the minimum energy, but the energy difference among *fcc*, *hcp*, and *bridge* sites was only  $\sim 1$  kcal/mol. Those sites were, therefore, considered to be isoenergetic. The S–Au distance calculated was 2.87 Å. In their calculations, the angle between Au surface normal and the S–C bond was constrained. Gronbeck *et al.*<sup>26</sup> performed QC calculations (DFT-BLYP) on a periodic system consisting of four (5×5) layers of dynamic Au atoms and one adsorbed CH<sub>3</sub>S- molecular chain, which was equiva-

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lent to low surface coverage of thiols on gold. A S–Au distance of 2.45 Å was obtained. The dynamic Au(111) surface simulated in the work allows the elongation of Au–Au lattice to a larger extent for this low surface coverage of thiols than for a full-surface coverage SAM. In the case of a full-surface coverage SAM, nearby thiols provide constraints to prevent a further elongation of Au–Au lattice. The Au–Au lattice distance obtained was 3.0–3.2 Å on the surface,<sup>26</sup> instead of 2.881 Å in the bulk. This larger elongation of Au–Au lattice gave rise to a shorter S–Au distance. Gronbeck *et al.*<sup>26</sup> showed that of a few geometrically reasonable positions for S (*fcc*, *hcp*, *atop*, and *bridge*), the *fcc* threefold hollow site was the most energetically favored. In addition, Yourdshahyan *et al.*<sup>27</sup> performed DFT calculations of CH<sub>3</sub>S in a (2×2) unit surface of Au(111). The difference in calculated energies among different adsorbed sites (*fcc*, *hcp*, *bridge*, and *atop*) is much larger than those previously reported.<sup>24,25</sup> A S–Au distance of 2.44 Å was reported at a surface coverage of 0.75. Kuger and Fuchs<sup>28</sup> did extensive DFT studies of short alkanethiols (methyl, ethyl, and n-propyl) on various Au clusters up to 5 Au atoms. Thus, it is desirable to perform *ab initio* quantum chemical calculations to study the binding of thiolate on Au(111) at a full surface coverage (preferably in a periodic system) and to reevaluate the Au–S distance.

Based on these previous *ab initio* QC calculations, several force fields were developed<sup>3,13,16,17,25</sup> and molecular dynamics (MD) simulations<sup>10–23</sup> using these force fields were performed on alkanethiol SAMs on Au(111) systems. In the earlier work by Hautman and Klein,<sup>10,11</sup> the interactions between S, –CH<sub>2</sub> and –CH<sub>3</sub> groups were treated in the united-atom (UA) approximation and the surface was modeled as a continuum interacting with pseudo-atoms via a structureless 12-3 potential. Later, Mar and Klein<sup>13</sup> used the all-atom representation and concluded that a herringbone arrangement of two chains per unit cell gave the most favorable packing structure in their molecular dynamic (MD) simulations. Pertsin and Grunze<sup>16</sup> used the all-atom chain model and a rigid but corrugated surface. In addition, they incorporated Au–S–C angle bend interactions based on quantum mechanical calculations of Sellers *et al.*<sup>24</sup> into their models. The first model featured a *sp*<sup>3</sup>-hybridization on sulfur with the equilibrium bond angle of Au–S–C of ~104°. The second model featured a *sp*-hybridization with the equilibrium bond angle of ~180°. Even with the Au–S–C potentials, only one and two chains per unit cell arrangements were found to be the most stable using the methods of stochastic global search and static energy minimization.<sup>16</sup> Bhatia and Garrison<sup>14</sup> used a dynamic Au(111) substrate, mobile sulfur headgroups, and the UA model in their MD simulations. Four structures of the c(4×2) superlattice of different length alkanethiols on Au(111) were proposed. However, two of them were stable only for a short time while the other two were stable only at lower temperatures (<100 K) and the orientations of the backbones of these two structures randomized at higher temperatures. Beardmore *et al.*<sup>25</sup> developed an empirical all-atom potential function to describe the alkanethiol headgroup-gold interaction potential surface. They found that the sulfur atoms in less densely packed regions did not reside in a single hollow site, but moved between adjacent

hollow sites as the SAM relaxed. In the case where complete monolayer coverage was assured, the packing of molecules would prevent movement of the headgroup. Li *et al.*<sup>17</sup> used the DREIDING force field modified to fit QC calculations to study the packing structures of alkanethiol SAMs on Au(111). This force field was modified to fit the QC calculation results by Sellers *et al.*,<sup>24</sup> in which the energy difference between *sp*- and *sp*<sup>3</sup>-hybridization modes was assumed to be zero. Unfortunately, none of the above models are able to reproduce the c(4×2) superlattice structure at ambient temperature as observed by various experimental techniques.<sup>4–9</sup> Gerdy and Goddard<sup>23</sup> developed a force field capable of predicting the c(4×2) structure based on a disulfide mode. There is a discrepancy in the literature about the existence of disulfide on Au(111).<sup>29,30</sup> Recent *ab initio* QC results by Gronbeck *et al.*<sup>26</sup> showed that disulfide was not stable as compared to thiolates on Au(111) surface. Thus, it is desirable to perform MD simulations of the c(4×2) superlattice structure of thiols/Au(111) with an accurate force field.

In this work, we performed *ab initio* QC calculations of alkanethiols on Au(111). Both clusters and periodic systems were used and no disulfide was considered. Based on the *ab initio* results, an accurate all-atom force field was developed. Molecular mechanics (MM) and MD simulations with the developed force field were performed on alkanethiol SAMs on Au(111) with different chain lengths to predict the c(4×2) superlattice structure at different temperatures.

## II. COMPUTATIONAL APPROACH

*Ab initio* QC calculations performed on clusters were based on density-functional theory (DFT)<sup>31</sup> with exchange-correlation functional in the local-density approximation (LDA) including gradient correction (BLYP). All *ab initio* calculations for the clusters were carried out using JAGUAR (version 4.0) from Schrödinger, Inc.<sup>31</sup> The basis set LACVP\*\* was used in QC calculations, where \*\* indicates the use of polarization functions. LACVP\*\* uses the Hay and Wadt<sup>32</sup> effective core potentials (ECP) for atoms K–Cu, Rb–Ag, Cs–La, and Hf–Au, and an all electron 6-31G basis description for atoms H–Ar and LAV3P for other atoms Zn–Kr, Cd–Xe, and Hg–Bi.<sup>31</sup> The clusters consist of CH<sub>3</sub>S-adsorbed onto Au(111) surface with two-layer Au atoms that are closest to the adsorbed site. In these *ab initio* calculations, dynamic or static Au atoms did not result in a significant difference in bond length and bond bending angle. To minimize the computational time, all *ab initio* QC calculations, unless specified, were done with fixed Au atoms. *Ab initio* calculations performed on periodic systems were also based on DFT with LDA. These calculations were carried out using Dmol<sup>3</sup> in CERIU2 (version 4.2) from Molecular Simulations Inc.<sup>33</sup> The basis set BNP was used.<sup>33</sup> The periodic systems were from the well-known closely packed ( $\sqrt{3} \times \sqrt{3}$ )R30° lattice on Au(111). Each periodic system consists of two-layer Au(111) surfaces and CH<sub>3</sub>S- group, which is adsorbed on different sites, such as *fcc*, *hcp*, *bridge*, and *atop* of Au(111) surface.

There are a few force fields<sup>13,16,17,25</sup> available for mo-

molecular simulations of alkanethiol SAMs on Au(111) developed based on earlier *ab initio* quantum chemical calculation results. Molecular simulations were performed using these force fields. However, none of these simulations are able to predict the  $c(4 \times 2)$  superlattice structure observed by experiments.<sup>4–9</sup> In this work, an all-atom model was used for hydrocarbon chains. The Morse potential was employed to describe interactions between S and Au, since it can mimic the bonding from a partially covalent bond,

$$E = De(\chi^2 - 2\chi), \quad (1)$$

where  $\chi = \exp[-S/2(R/Re - 1)]$ . The equilibrium position  $Re$  was determined to fit the *ab initio* interatomic S–Au distance. The dissociating energy  $De$  and the scale factor  $S$  were determined to fit the binding energy of thiolate with Au and the energy difference for a thiol adsorbed on different sites (*fcc*, *hcp*, *atop*, and *bridge*). The parameter fitting was carried out on POLYGRAF.<sup>34</sup> Interactions for C–H, C–C, H–H, C–S, H–S, C–Au, and H–Au were described by the Lennard-Jones (LJ) 12-6 potentials. The parameters for the LJ12-6 potentials were obtained from the universal force field (UFF).<sup>35</sup> Previously, we successfully searched for an optimal packing structure of alkyl monolayers on Si(111).<sup>36</sup> Similarly, in this work five possible initial structures for each chain length ( $C_1$ – $C_{18}$ ) were constructed based on molecular packing structures and orientations of alkanethiols on Au(111). The optimal structure is the one with the lowest energy among these minimized structures. To see the  $c(4 \times 2)$  superlattice under experimental conditions, MD simulations were performed on the optimized molecular packing structures at different temperatures. Three-dimensional periodic boundary conditions (PBC) were applied to these systems. A vacuum size of 20 Å in height was placed on top of the monolayers.<sup>36,37</sup> The molecular structures from MD simulations were analyzed to obtain molecular orientations, system tilt angles, and monolayer thickness. The simulation results were then compared to those from experimental measurements.

### III. RESULTS AND DISCUSSION

#### A. *Ab initio* quantum chemical calculations

##### 1. Periodic systems

Gronbeck *et al.*<sup>26</sup> used a low-surface coverage of thiol on Au(111) in periodic systems, where all Au atoms were allowed to move. A larger elongation of Au–Au lattice was obtained (3.0–3.2 Å), which in turn leads to a shorter S–Au distance (2.45 Å). In this work, periodic systems consist of two-layer Au atoms. Thiol is placed at different adsorption sites (*hcp*, *fcc*, *bridge*, and *atop*), as illustrated in Fig. 1, corresponding to a full surface coverage. Results including the S–Au distances and energy differences among different adsorption sites are also presented in Table I. The S–Au distance is 2.734 Å for the *fcc* and 2.736 Å for the *hcp*. The energy of the system with the *fcc* adsorption site is lower than that of the *hcp* site by 0.90 kcal/mol. The systems with *atop* and *bridge* adsorption sites have higher energies. These results show that the lowest-energy adsorption site of thiol on Au(111) is the *fcc* site, in a good agreement with the

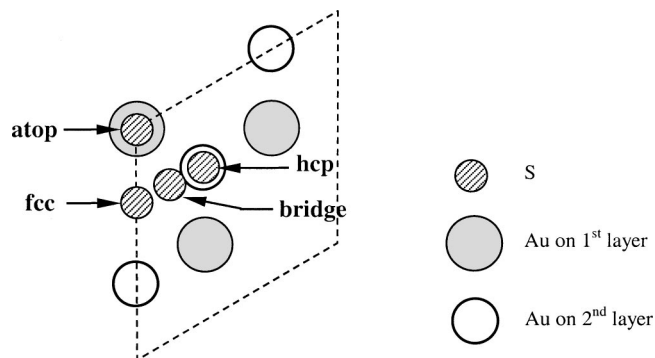


FIG. 1. An illustration of adsorption sites (*fcc*, *hcp*, *atop*, and *bridge*) of  $\text{CH}_3\text{S}^-$  on Au(111) surface in a periodic system for *ab initio* quantum chemical calculations.

previous QC results.<sup>24–26</sup> *Ab initio* results obtained from this work for periodic systems were used for force field development.

##### 2. Clusters

The clusters used in the previous work<sup>24,25</sup> might be too small to represent Au(111) surface.<sup>26</sup> In addition, these clusters were not symmetric. In this work, *ab initio* quantum chemical calculations were also performed on the clusters shown in Fig. 2. Cluster A consists of 15 Au atoms in two layers and a thiol seated onto the *fcc* site (S atom directly above a threefold hollow site with no Au atom in the second layer beneath the S atom), while cluster B includes 13 Au atoms in two layers and a thiol adsorbed on the *hcp* site (S directly above a threefold hollow site with an Au atom in the second layer beneath the S atom). These two clusters are symmetric. Energies for the two clusters from *ab initio* QC calculations are also listed in Table I. The energy for the *fcc* site is lower than that of the *hcp* site by 0.72 kcal/mol. The S–Au distance changes from 2.789 to 2.734 Å when the adsorption site of  $\text{SCH}_3^-$  on Au(111) is changed from the *fcc* to the *hcp*. When Au atoms of the nearest neighbors around the S atom in the first layer were allowed to relax and those Au atoms of the outer layer were fixed, it was found that the S–Au distance decreased by  $\sim 0.1$  Å for both *fcc* and *hcp* clusters. The decrease of the S–Au distance results from the elongation of Au–Au lattice. The lattice distance between movable Au atoms was 2.97 Å, which is smaller than that from the work by Gronbeck *et al.*<sup>26</sup> The difference in energy between the *fcc* and the *hcp* sites from the cluster is very close to that from the periodic systems.

TABLE I. *Ab initio* QC results for both periodic systems and clusters.

Clusters	<i>fcc</i>	<i>hcp</i>		
Bond length <sup>a</sup> (Å)	2.789	2.734		
Energy <sup>b</sup> (kcal/mol)	0.0	0.72		
<i>Periodic Systems</i>				
	<i>fcc</i>	<i>hcp</i>	<i>bridge</i>	<i>atop</i>
Bond length <sup>a</sup> (Å)	2.734	2.736	2.659	2.530
Energy <sup>b</sup> (kcal/mol)	0.0	0.90	2.92	4.03

<sup>a</sup>Distance between S and Au.

<sup>b</sup>Energy for the system of methylthiols on Au(111).

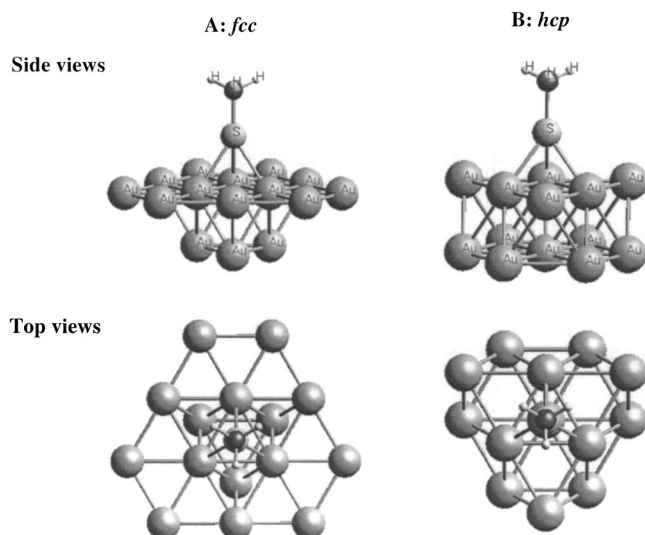


FIG. 2. Clusters A (*fcc*) and B (*hcp*) for *ab initio* quantum chemical calculations.

## B. Force field development and molecular mechanics

*Ab initio* results for both clusters and periodic systems clearly show that the *fcc* adsorption site has the lowest energy. Since force field development was done with periodic systems, the S–Au distance of 2.734 Å from the periodic system with the *fcc* site was chosen. The binding energy of thiolate with Au(111) surface was –44.0 kcal/mol from adsorption measurements.<sup>38</sup> Interestingly, x-ray photoelectron spectroscopy (XPS) study by Castner *et al.*<sup>39</sup> and Ishida *et al.*<sup>40</sup> also showed that the binding energy of thiolate with Au(111) surface was about –1.9 eV (–43.7 kcal/mol). An all-atom model was used for hydrocarbons. The parameters for hydrocarbons were from the UFF.<sup>35</sup> The Morse potential model was used to describe interactions between S and Au. The parameters for the Morse potential were fitted to bond length, binding energy, and energy difference between adsorption sites. Three parameters of the Morse potential model were obtained:  $Re = 2.903$  Å,  $De = 3.182$  kcal/mol, and  $S = 8.0$ . The S–Au distances, binding energies for *fcc* and *hcp*, and the energy difference between them from the force field along with their QC results are listed in Table II. The results showed that the developed force field for alkanethiols on Au(111) were able to fully reproduce *ab initio* and experimental results.

TABLE II. Comparison of properties from the developed force field (MSX) and from *ab initio* QC calculations for periodic systems.<sup>a</sup>

Site	S–Au distance, Å		Energy difference, kcal/mol	
	MSX	QC	MSX	QC
<i>fcc</i>	2.734	2.734	0	0
<i>hcp</i>	2.734	2.736	0.84	0.90

<sup>a</sup>Binding energy for methylthiols on Au(111) is –44.0 kcal/mol from experiment (Ref. 38) which was reproduced by the developed force field in this work (–44.01 for the *fcc* site and –43.06 for the *hcp* site).

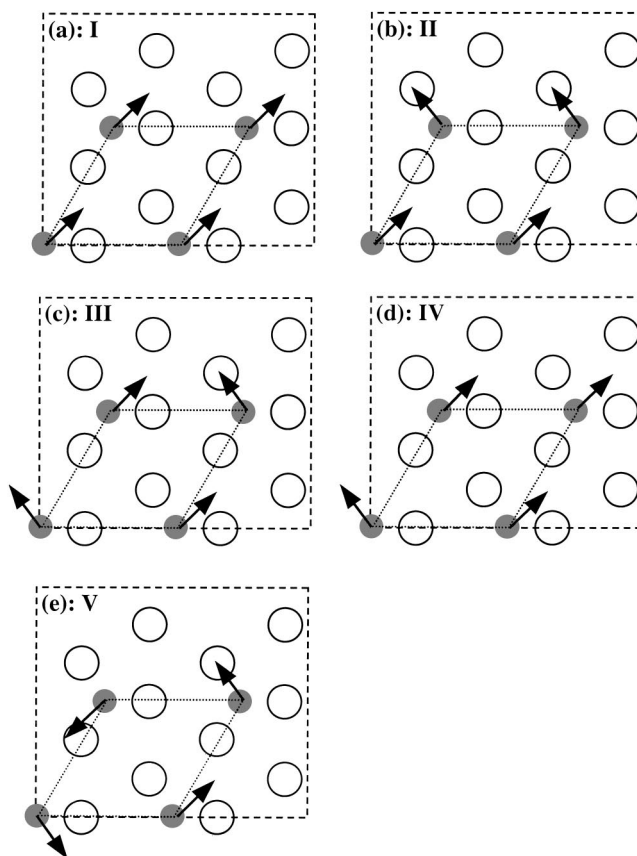


FIG. 3. Five possible initial packing structures of alkanethiol on Au(111). The arrows represent the orientations of hydrocarbon chains. Open circles represent Au atoms, while solid circles S atoms. One chain per unit cell in packing I, two chains per unit cell in packing II (herringbone), and four chains per unit cell in packings III–V. The structures of packings III and IV are the so-called  $c(4 \times 2)$  superlattice structure.

The closely packed structure of alkanethiol SAMs on Au(111) is a hexagonal  $(\sqrt{3} \times \sqrt{3})R30^\circ$  lattice in which a thiol is seated on a threefold hollow site of the surface. This structure has been confirmed by scanning probe microscopy (SPM).<sup>1–3</sup> Since molecular chains on Au(111) surface could be packed in different orientations, the  $c(4 \times 2)$  superlattice of the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  lattice could be formed, such as the ones shown in Figs. 3(c) and 3(d), in which four chains are packed in two orientations as indicated by arrows. Molecular orientation was defined by the projection of the plane of the *all-trans* hydrocarbon backbone.<sup>7,14</sup> The  $c(4 \times 2)$  superlattice structure has been confirmed by experiments.<sup>4–9</sup> In order to predict the  $c(4 \times 2)$  superlattice structure, a simulation cell of the superlattice, illustrated in Fig. 4, was used to perform molecular simulations. The size of the simulation cell is  $9.99$  Å  $\times$   $8.652$  Å. There are four chains placed on the threefold hollow sites in this cell. When alkanethiol molecules are chemisorbed on Au(111), possible orientations for molecular chains are the nearest-neighbors (NN or the first neighbors), the next-nearest neighbors (NNN, or the second neighbors), and the next-next-nearest neighbors (NNNN or the third neighbors). Based on these orientations, five possible initial packing structures of alkanethiols on Au(111) were constructed. The initial packing structures are shown in Figs. 3(a)–3(e). Each simulation cell has the same size and con-

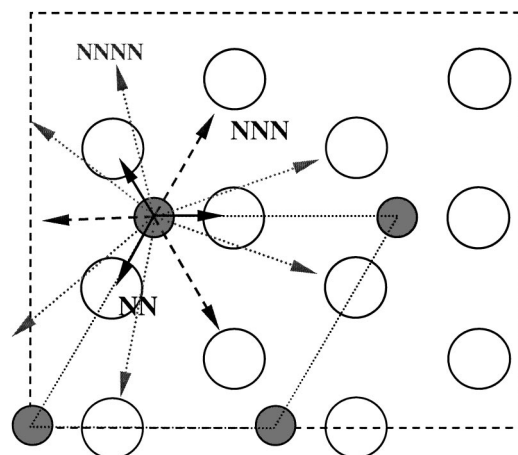


FIG. 4. Molecular orientations of one alkanethiol chain on Au(111) in a simulation cell with a dimension of  $(9.99 \text{ \AA} \times 8.652 \text{ \AA})$ . The rhombus outlined by dotted lines is the basic  $\sqrt{3} \times \sqrt{3} R30^\circ$  structure. Open circles represent Au atoms, while solid circles S atoms. The arrows depict the orientations: The nearest neighbors (NN), The next-nearest neighbors (NNN), and the next-next-nearest neighbors (NNNN).

tains four molecular chains, but the *unit cell* for each packing structure is different. The packing **I** has only one chain per unit cell, while the packing **II** two chains per unit cell. For packings **III–V**, each unit cell contains four chains. MM simulation approach with the developed force field was then applied to minimize the initial packing structures of **I–V** with different chain lengths ( $C_1$ – $C_{18}$ ). The energies of the minimized structures are listed in Table III. As shown, the energy for the packing structure **III** is the lowest for all chain lengths studied. Thus, the packing **III** is the optimal structure, for which all S atoms sit on the *fcc* site. Figure 5(a) shows the packing structure **III** for  $C_{18}$  chain length. The backbones of four molecular chains are *all-trans*. The top view of the molecular packing structure in Fig. 5(b) shows the molecular orientations of four molecular chains on Au(111). These four molecular chains have two orientations: Two molecular chains orient toward NN and the others orient toward NNN. The arrows, which depict the orientations in Fig. 5(b), also represent the project of the planes of the *all-trans* hydrocarbon backbones. As shown in Fig. 5(c), twist angles are  $\sim 0^\circ$  for two alkanethiol chains and  $\sim 90^\circ$  for another two chains. The twist angles distinguish the two symmetrically nonequivalent pairs of the alkanethiol chains per unit cell. The packing **III** shown in Fig. 5 is the so-called

TABLE III. Energies of different minimized structures from packings **I–V** for various chain lengths, kcal/mol.

Chain length	<b>I</b>	<b>II</b>	<b>III</b>	<b>IV</b>	<b>V</b>
$C_1$	0.32	0.58	0.00	0.47	0.30
$C_2$	...	1.31	0.00	0.26	0.86
$C_4$	2.41	3.45	0.00	0.30	2.68
$C_6$	5.46	2.16	0.00	0.17	6.47
$C_8$	8.95	3.35	0.00	0.06	10.99
$C_{10}$	12.27	1.34	0.00	0.04	15.65
$C_{12}$	15.27	1.82	0.00	0.08	20.24
$C_{16}$	20.70	2.78	0.00	0.23	29.25
$C_{18}$	23.29	3.26	0.00	0.30	35.12

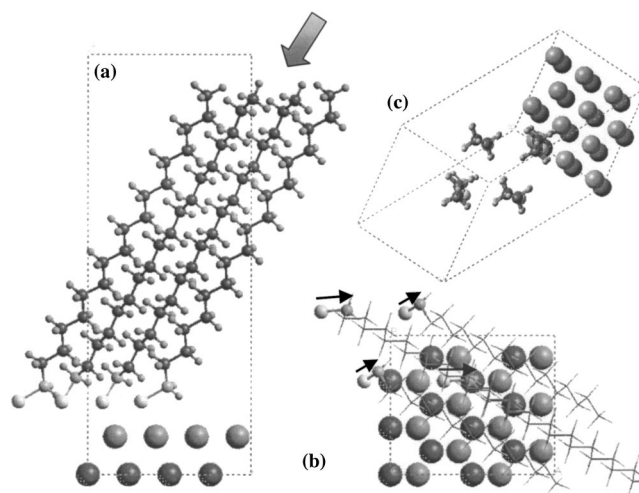


FIG. 5. (a) Side, (b) top, and (c) angled views of  $C_{18}$  alkanethiol SAMs on Au(111) for the packing **III** by MM simulations with the developed force field. The angled view shown in (c) is from the direction indicated by the shaded arrow in (a). The arrows on the top view represent the orientation directions from S to the first C in molecular chains. Since the structure of hydrocarbon chains are *all-trans*, the arrows also represent the projects of planes of backbones of the chains.

$c(4 \times 2)$  superlattice structure. This  $c(4 \times 2)$  superlattice is also found for other chain lengths. For the packing **III**, the angles of surface-S-C were  $145.6^\circ$  for two chains and  $119.2^\circ$  for another two chains. For the basic  $(\sqrt{3} \times \sqrt{3}) R30^\circ$  lattice of alkanethiol on Au(111), the angle of surface-S-C was  $112.0^\circ$ . Recent experiments by Zharnikov *et al.*<sup>41</sup> showed that the angle of surface-S-C was  $\sim 104^\circ$  for *all-trans* 4,4'-biphenyl-substituted alkanethiol (BPAT) SAMs on Au.

The energies in Table III show that the packing **IV** has very comparable energies to the packing **III** for each chain length. The energy differences between packings **III** and **IV** are smaller than  $kT$  ( $\sim 0.6$  kcal/mol at 300 K). Thus, the packing **IV** is one of the possible packing structures for alkanethiols–Au(111) at room temperature. Both packings **III** and **IV** were observed experimentally using STM.<sup>6</sup> Several slightly different adsorption geometries in alkanethiol–Au were observed from synchrotron-based high-resolution x-ray photoelectron spectroscopy (HRXPS) by Heister *et al.*<sup>42</sup> Figures 6(a) and 6(b) show the molecular structure of  $C_{18}$  alkanethiol on Au(111) from the packing **IV**. Similar to the packing **III**, the backbones of four molecular chains are *all-trans* and two molecular orientations of four molecular chains on Au(111) were found: One molecular chain orients toward NN, whereas the other three molecular chains orient toward NNN.

### C. Molecular-dynamics simulations

In order to compare with the experimental results directly, MD simulations with the developed force field were carried out on the minimized structures from the packing **III** for each chain length at 300 K. In MD simulations, all S atoms were initially put on the *fcc* sites (based on *ab initio* calculations above) and allowed to move. However, they stayed around the *fcc* sites within  $0.19 \text{ \AA}$  and did not diffuse to the *hcp* sites. It was found that the  $c(4 \times 2)$  structure from

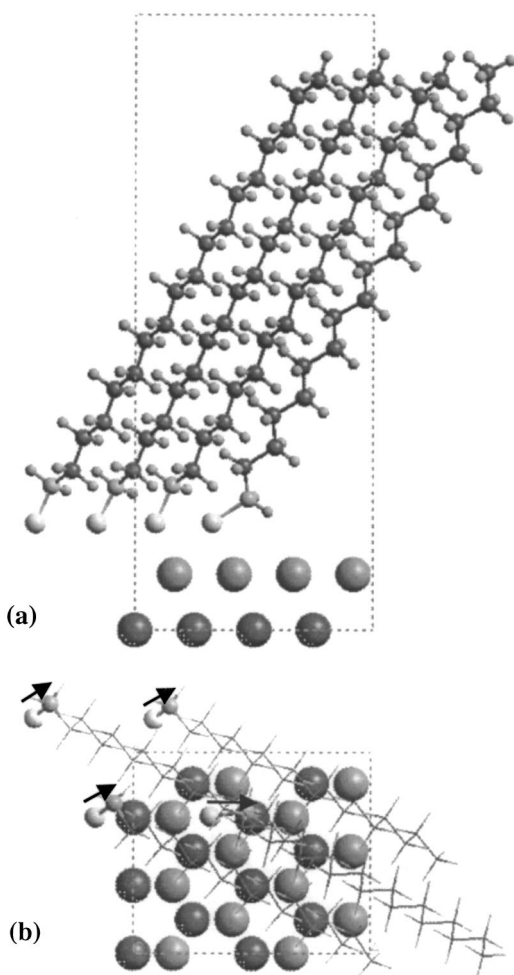


FIG. 6. (a) Side and (b) top views of  $C_{18}$  alkanethiol SAMs on Au(111) for the packing **IV** by MM simulations with the developed force field. The arrows on top view represent the orientation directions from S to the first C in molecular chains and the projects of planes of backbones of hydrocarbon chains.

MD simulations is similar to that from MM simulations. Molecular orientations for four chains are the same as those shown in Fig. 5(b). MD simulations also showed that for larger systems (16 chains in a simulation cell) at 300 K there coexists of packings **III** and **IV**, which is due to the fact that packings **III** and **IV** have a very close energy (cf. Table III). Figures 7(a) and 7(b) represent packings **III** and **IV** extended in two dimensions, respectively. The packing **III** forms a zigzaglike structure, while the packing **IV** forms a diamond-like structure. The packing **III** was observed by our STM experiment on  $C_{12}$ -alkanethiol SAMs/Au(111) formed in 1.0 mM ethanolic solution preheated to 70 °C and kept in an oven at 70 °C for 2 hours,<sup>43</sup> as shown in Fig. 8. The  $c(4\times 2)$  superlattice structures of packings **III** and **IV** were also observed by other STM experiments.<sup>6</sup> Bhatia and Garrison<sup>14</sup> proposed four  $c(4\times 2)$  superlattice structures of alkanethiols on Au(111). However, two of them were stable only for a short time while the other two were stable only at lower temperatures ( $<100$  K). MD results from this work showed that the force field developed in this work is capable of predicting the  $c(4\times 2)$  superlattice structure.

Klein and co-workers<sup>11</sup> found the temperature depen-

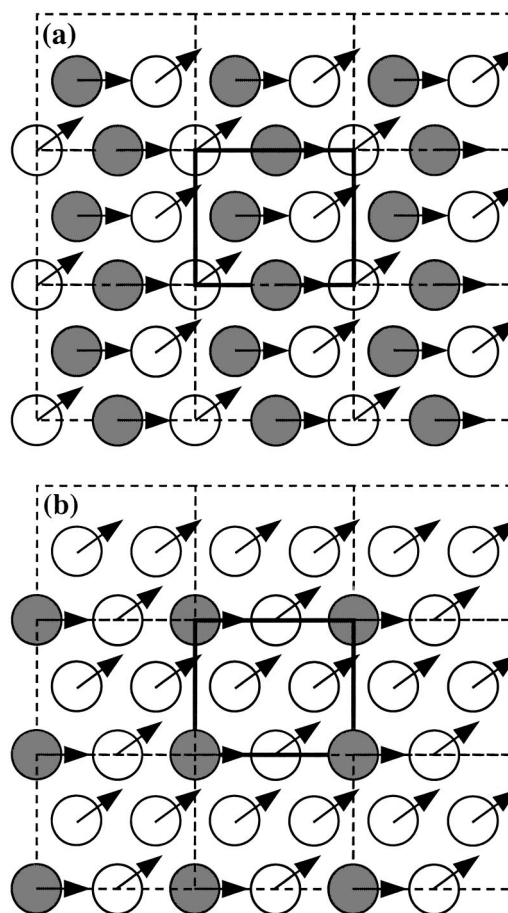


FIG. 7. The  $c(4\times 2)$  superlattice structures of (a) the packing **III** and (b) the packing **IV** for  $C_{12}$  alkanethiol SAMs on Au(111) predicted by MM simulations with the developed force field.

dence of various properties of alkanethiols–Au(111) monolayers, such as tilt angle, monolayer thickness, and conformation. Thus, MD simulations with the developed force field were carried out on the structure of packing **III** for  $C_{12}$  alkanethiol SAMs on Au(111) at temperatures ranging from 50 to 400 K. Generally, system tilt angle becomes smaller as

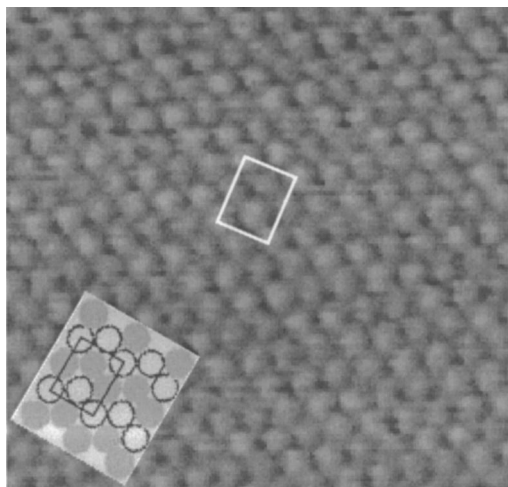


FIG. 8. The packing **III** illustrated by the insertion can be seen from the STM image ( $8\times 8$  nm) of  $C_{12}$ -alkanethiol SAMs on Au(111) (Ref. 43).

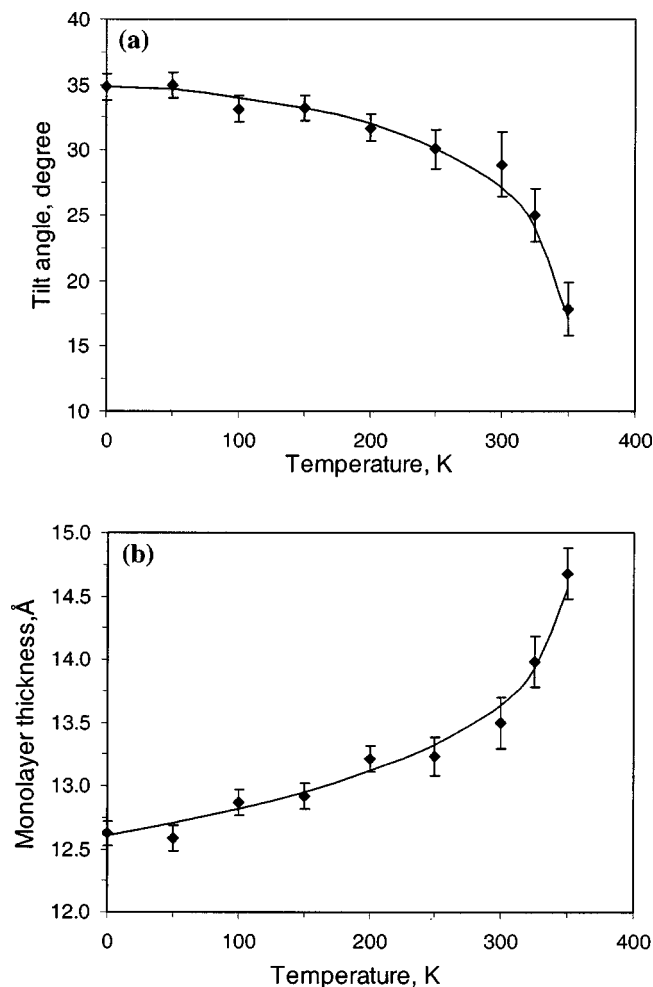


FIG. 9. (a) System tilt angle and (b) monolayer thickness of  $C_{12}$  alkanethiol SAMs on Au(111) from MD simulations with the developed force field at various temperatures.

temperature increases. Smaller tilt angle results in thicker monolayers. System tilt angle is the one between surface normal and the vector from head to tail group of a molecular chain. Monolayer thickness is determined by averaging the Z-coordinate (height) of the topmost C atom in molecular chains. The tilt angle and the monolayer thickness are plotted as a function of temperature in Figs. 9(a) and 9(b), respectively. It was found from MD simulations that as temperature rises, tilt angle decreases, whereas monolayer thickness increases. Similar results were also obtained by Klein and co-workers.<sup>11</sup> From MD simulations at room temperature (300 K), tilt angle was  $\sim 29^\circ$  and monolayer thickness was  $\sim 13.5$  Å. The results are in good agreement with those from experimental measurements for  $C_{12}$  alkanethiol SAMs on Au(111).<sup>3</sup> When temperature was beyond 350 K, both tilt angle and monolayer thickness had significant changes. It was found from MD simulations that molecular packing structures at higher temperatures became disordered. The carbon backbone in molecular chains was not *all-trans*; some *gauche* defects were observed at higher temperatures. Experiments have shown that alkanethiol SAMs on Au(111) are not stable at higher temperatures. When temperature reaches  $\sim 100^\circ\text{C}$ , molecular chains begin to desorb from the sub-

strate surface.<sup>3</sup> For a chain length up to 18, the tilt angle varies ( $32 \pm 1.5^\circ$ ) at 300 K from molecular simulations, which agrees well those from experiments.<sup>44</sup> Experimental results<sup>44</sup> show that the tilt angle depends on chain length for a chain length beyond 18.

#### IV. CONCLUSIONS

In this work, *ab initio* quantum chemical calculations were performed on both clusters and periodic systems of methylthiols on Au(111). Based on *ab initio* results (the S–Au distance and energy differences among adsorption sites) for periodic systems and experimental data (binding energy), an accurate all-atom force field for alkanethiols on Au(111) was developed. MD and MM simulations were carried out based on the developed force field to study the  $c(4 \times 2)$  superlattice structure of alkanethiol SAMs on Au(111) for various chain lengths at a wide range of temperatures. Simulation results showed that the packing **III** has the lowest energy and the packing **IV** has a slightly higher energy than the packing **III**. Both packings **III** and **IV** are the so-called  $c(4 \times 2)$  superlattice structure. MD results showed that the tilt angle decreases as temperature increases, whereas the monolayer thickness increases. The accurate force field developed in this work is useful to molecular simulation studies of various systems involving alkanethiol SAMs on gold surfaces.

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