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Atomistic Structure for Self-Assembled Monolayers of Alkanethiols on Au(111) Surfaces

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Abstract: Using force fields based on quantum mechanics, we calculate the stable crystal structure for decanethiol dimers on Au(111) surfaces. We find that the optimum structure leads to an X-ray diffraction pattern identical with that recently determined by Eisenberger and co-workers. This confirms the *c*(4 × 2) cell determined using He and X-ray diffraction, providing the first atomistic structural description of a self-assembled monolayer (SAM). The excellent agreement between theory and experiment suggests that theory could be used to predict structures for new SAMs, allowing the design to be carried out in advance of experiment.

Self-assembly of molecules provides one of the most promising approaches to synthesizing nanoscale devices (spatial sizes of 10 nm or below).[1] Of particular interest are the self-assembled monolayer (SAM) two-dimensional nanostructures.[2−7] Starting with early work involving alkanethiols on Au(111),[8−10] simple straightforward methods have been developed for preparing well-ordered monolayers and multilayers. There remain, however, a number of uncertainties about the structural characteristics of these films. Indeed, for the original alkanethiols, the chemical character of the sulfur atom at the gold surface was not established. The starting material is an alkanethiol **1a**. It was widely thought that the thiols deprotonate at the surface, leading to thiolates **1b**,[1,2,8] but there was little direct evidence for this view. Some vibrational evidence indicated that the thiols might form disulfides **1c** at the surface (using EELS, Nuzzo and co-workers[9] observed $S-S$ stretch and $C-S-S$ bend vibrations); however, the results were not consistent over samples.

RSH **1a**

RS^- **1b**

$RSSR$ **1c**

$$R = -(CH_2)_{n-1}(CH_3)$$

A breakthrough concerning the structure of these systems was reported recently (December 1994) in *Science* by Eisenberger and co-workers.[14] Using grazing-angle X-ray diffraction of well-annealed overlayers of decanethiols on Au(111), they were able to establish that these thiols form *dimers* **1c**, packed into a two-dimensional crystal structure commensurate with the Au(111) substrate. This leads to a *c*(2 × 4) unit cell with the alkane tails canted by $\theta = 37° \pm 2°$ from the surface normal. Although the data do not determine the atomic details, they do establish that the all-trans alkane tails form a pseudo-closest-packed array with a structure *different* from the normal orthorhombic polyethylene crystal (confirming earlier work by Scoles and co-workers[19]).

These experiments stimulated us to examine the detailed atomic arrangements using molecular dynamics and molecular mechanics simulations. For these studies we started with the DREIDING[15] force field (FF) but modified the $S-S$ dihedral potential to match the rotational barrier calculated from quantum chemistry (QC) studies[16] of diethyl disulfide (this is denoted D/S). Second, we modified the alkane part of this force field to match one developed[17] for the polyethylene crystal. This is denoted as D/S,PE. We expect S to prefer binding to 3-fold hollow sites on the surface. This was incorporated into the force field by using a bond interaction from each sulfur atom to a gold atom one layer down from the surface.

First, we examined the isolated alkanethiol dimer **1c**. We found the parallel structure in Figure 1 where the top view shows that the two alkane tails are parallel and in contact while the bottom view (looking *along* the direction of the alkyl tail) shows that the two parallel all-trans chains have perpendicular CC planes. The two chains have average $C-C$ contacts of 4.4 Å (the contact distances between interior hydrogens is about 2.9 Å). Forcing the $C-C$ planes to be *parallel* and minimizing the structure lead to an energy 3.0 kcal/mol higher than that in Figure 1, and we did not consider this further.

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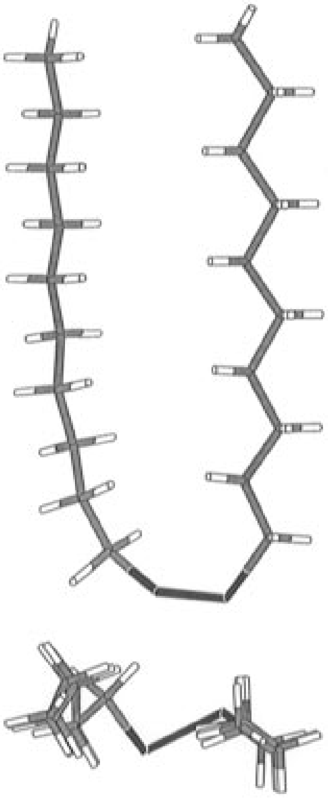

Figure 1. Optimum *parallel* structure of the decyl sulfide dimer. Here the two alkyl tails are parallel, but the *CC* planes of these tails orient perpendicularly with an average separation of 4.4 Å. The bottom view is rotated from the upper view by 90° about the horizontal axis. The sulfur atoms are black, the carbon atoms are gray, and the hydrogen atoms are white.

The second important structure for **1c** has the all-trans chains splayed away from each other. The van der Waals contacts favor the parallel structure (Figure 1), stabilizing it by 0.67 kcal/mol for each carbon added to both chains. On the other hand, the splayed structure minimizes strain in the $C-S-S-C$ turn while the parallel structure has 3.0 kcal/mol of strain energy in the turn. For chain lengths longer than 13, the parallel structure is favored. For the chain length of 10 used here and in the X-ray study,[14] the splayed structure is favored by 1.85 kcal/mol. However, the parallel structure should lead to much greater bond energy to the Au surface, stabilizing it over the splayed structure (which is also disfavored by the small saturation coverage). In addition, the packing energy of the monolayer stabilizes the parallel dimer by an additional 18 kcal/mol per dimer.

In order to understand how these disulfide units pack to form a dense monolayer, we first examined the structures and energetics for various packings of infinite all-trans alkyl chains to form polyethylene crystals. As indicated in Figure 2, there are two simple classes:

(1) *L* with all *CC* planes parallel, and (2) *T* with half the *CC* planes perpendicular to the other half. Each arrow in Figure 2 represents the orientation of the alkyl tail. The *CC* plane lies in the plane indicated by the arrow, and the arrowhead shows the phase of a CH_2 in this plane. These calculations indicate a number of *L* and *T* type structures with comparable energies (see Table 1). *T* is the observed structure of PE. Including zero point energy, the experimental cohesive energy at 0 K for PE is 2.02 kcal/mol,[17] in good agreement with these calculations (2.07 kcal/mol).

The restriction that pairs of adjacent chains have perpendicular *CC* planes (in order to attach to the $S-S$ linkage) restricts SAM considerations to the *T* and *T** structures. The energies of the optimized structures for various packings of thiol dimers on Au(111) are given in Table 2. *T** is lowest, and the optimum *T** structure is shown in Figure 3. The alkane tails leads to a *c*(4 × 2) pattern with pseudo-close-packing. This compares well with the X-ray diffraction[14] and He diffraction[19] studies which determined that a monolayer of alkanethiol on Au(111) has the *c*(4 × 2) packing corresponding to our *T** structure. The theory finds the alkanethiols to be canted at an angle to the surface normal of $\theta = 28.3 \pm 1.5°$ (the canting is parallel to the *a* axis). Reference 14 reports $\theta = 37 \pm 2°$ with a setting angle (the rotation angle of the symmetry plane of the tail about its axis) $\phi = 21°$; however, details of how this is obtained from the data are not provided.

Table 1. Cohesive Energy (kcal/mol per CH_2) of Polyethylene Crystals

	cohesive energy		structure			
lattice	D/S[d]	D/S,PE[d]	*a* (Å)	*b* (Å)	γ (deg)	ϕ[c] (deg)
*L*11	2.14	2.08	4.27	4.74	120	35.9
*L*12	1.99	2.02	4.96	8.06	120	10.9
*L*22	2.03	2.06	8.03	10.28	120	6.2
T[a]	2.09	2.07[b]	7.19	4.81	90	42.0
*T**	1.98	2.00	7.29	9.73	90	43.3

[a] This corresponds to the observed orthohombic structures of PE. [b] The experimental value 2.02 kcal/mol (see ref 17). [c] Setting angle. [d] The force field; see the text.

Table 2. Cohesive Energy and Structure of Alkyl Sulfide Dimer Monolayers

structure	cohesive[a] energy	unit cell	canting[b] (deg)
*L*12	17.16	(1 × 2)	26.2 ± 1.2
*L*22	15.43	(2 × 2)	26.5 ± 2.2
T	18.42	(1 × 2)	26.7 ± 0.5
*T**	18.64	*c*(2 × 4)	28.3 ± 1.5

[a] kcal/mol per dimer. [b] Calculated by using the last four carbons of each chain.

We show in Figure 4a the X-ray diffraction intensities predicted from the *T** structure (this pattern is for an out-of-the-plane momentum of $Q_z = 0.1/A$ in order to compare directly with experiment). The experimental diffraction pattern is shown in Figure 4c where we see an excellent fit with the predictions for *T**. In particular, both theory and experiment find systematic extinctions for (1, 0) and (0, 1). Due to the canting of the alkyl tails (and the nonzero Q_s), the theory gives slightly different intensities in the four quadrants of Q_x, Q_y. Averaging over these four quadrants leads to Figure 4b which has intensities in excellent agreement with experiment (Figure 4c). The slight differences might be because the theory is for $T = 0$ K while the experiment is for $T = 300$ K.

Thus, we conclude that the lowest energy *T** structure predicted from the theory is identical to the fully annealed structure observed by experiment. This is very encouraging because it indicates that theory might be used to predict the most stable structures *in advance of experiment*. This would be essential for designing new nanostructures where one might choose the support, structure of the overlayer, and additives to optimize the properties.

The procedure for predicting the structure for a new SAM can be illustrated for the case considered herein. In the *T* structure, each alkane tail has six neighbors (pseudo-close-packing) with four at 4.35 Å and two at 4.81 Å. In *T** there are four neighbors at 4.38 Å and two at 4.87 Å. For Au(111) the nearest neighbor spacing is 2.87 Å, too small for the alkanethiols. The smallest spacing of Au(111) compatible with the alkane spacing is 4.97 Å. Thus, we would expect the dimer

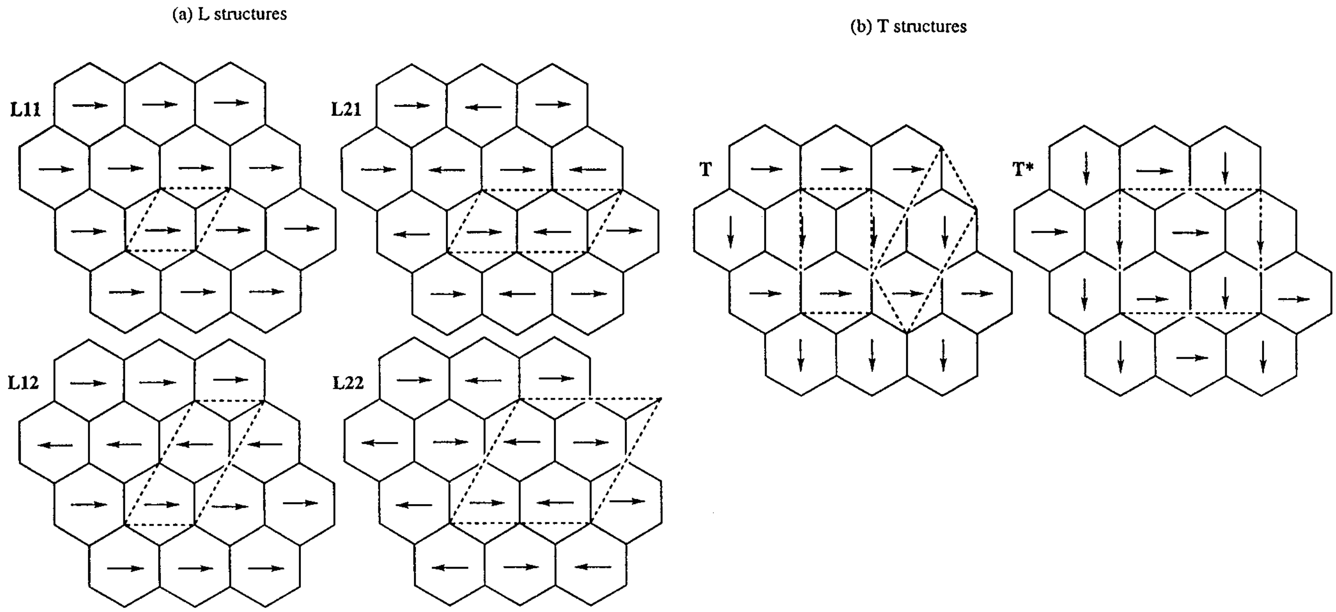

Figure 2. Stable packings of infinite alkyl chains. The arrows represent the *CC* planes of the alkyl tails, and the direction of the arrow is the phase of the tail. The structures in (a) have all planes parallel and are labeled *L*. The structures in (b) have half the *CC* planes perpendicular to the other half and are denoted as *T*. In these structures the setting angle (ϕ) of one *CC* plane is taken in the *a* direction. This setting angle (see Table 2) is optimized in each case to obtain the optimum structure. The structure *T* in (b) corresponds to the observed orthorhombic structure of PE (observed $\phi = 41°$ for $T = 300$ K, calculated $\phi = 42°$ at 0 K).

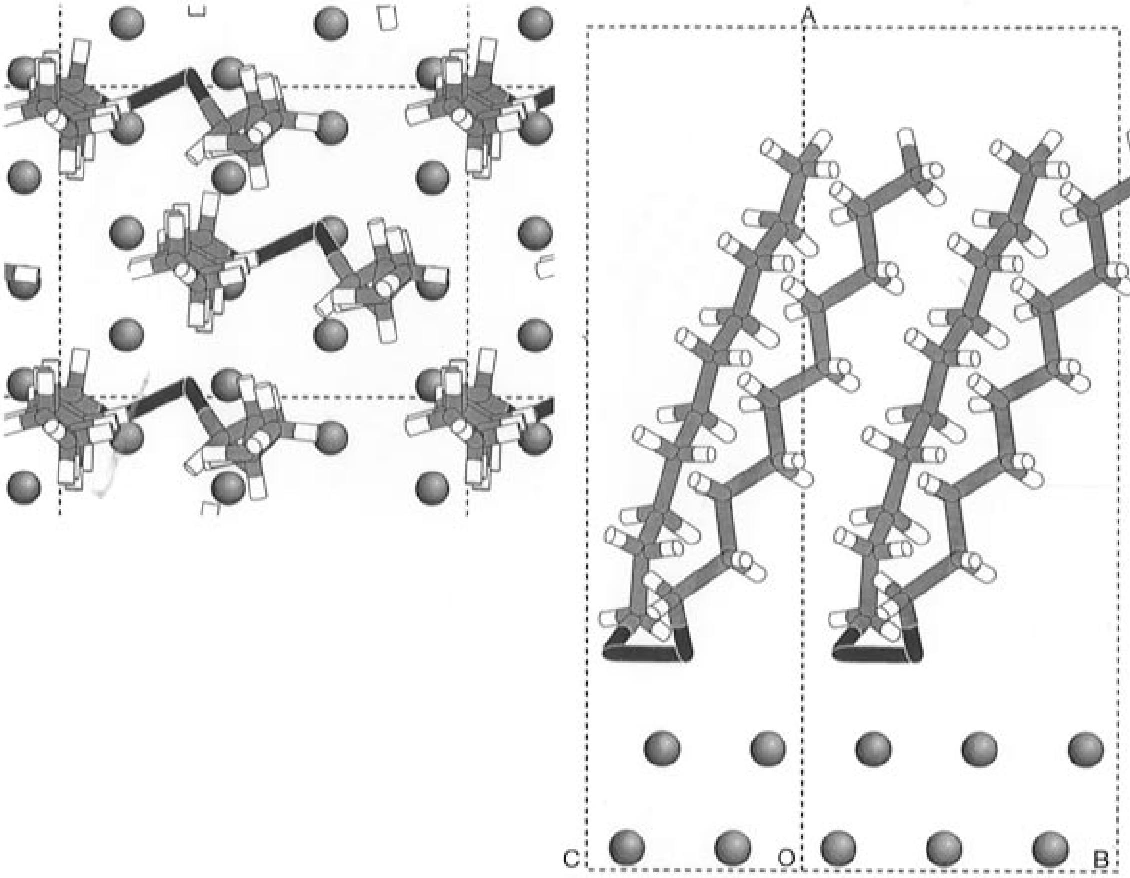

Figure 3. Optimum structure of the *T** SAM. The gold atoms are round, the sulfur atoms are black, the carbon atoms are gray, and the hydrogen atoms are white. (b, right) shows the side view oriented to show the two dimers per unit cell with their *CC* planes parallel or perpendicular to the view. (a, left) is a top view but oriented *along the alkyl chains* (at a canting of 28.3° from the normal) to compare with the idealized structures in Figure 2.

to orient so that the two neighbors preferring 4.81 or 4.87 Å increase this spacing slightly to attain 4.97 Å. This might require less strain for *T**, perhaps explaining its preference over *T*. With some spacings increased from 4.87 to 4.97 the others should decrease from 4.38 to 4.35 Å (assuming constant area per alkane). In order to match the spacings of Au(111), this requires canting of the alkanethiols. The amount of canting can be predicted by assuming the spacing of 4.35 Å. This leads

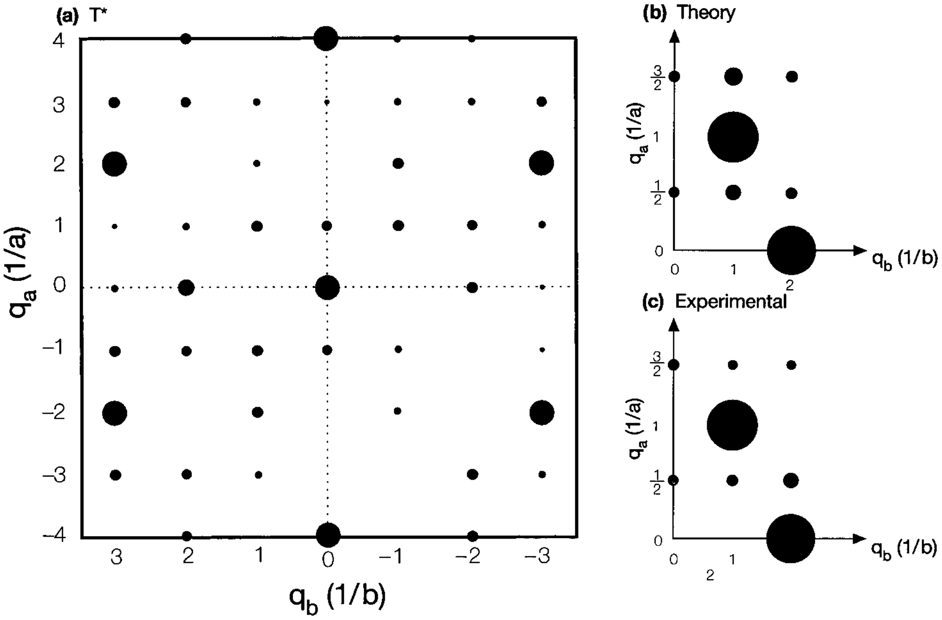

Figure 4. X-ray diffraction patterns. (a) Shows the predicted diffraction pattern[20] for the optimized monolayer with the *T** structure. (b) Averages the predicted pattern over the four quadrants of (a). (c) Is the experimental pattern adapted from ref 14.

to a projected spacing of 3.77 = 4.35$\sqrt{3}/2$ (where the geometric factor corrects for the distance perpendicular to the canting plane). The spacing of Au atoms is 4.97$\sqrt{3}/2$ = 4.30. Thus, the canting angle is $\cos\theta = 3.77/4.30$ or $\theta = 28.7°$. The optimum angle calculated from the simulations is $\theta = 28.3°$, in excellent agreement. Starting with this packing, we would carry our molecular dynamics studies to obtain the optimum structure and properties. To consider a different alkanethiol, say polypropylene (PP), poly(vinyl chloride) (PVC), poly(tetrafluoroethylene) (PTFE), or nylon, we would first consider the packing of the isolated chains (from theory or experiment). Using these spacings, we would consider the minimum spacing for attachment to the support. On this basis, we would terminate the alkyl chain with a suitable group for self-assembled attachment to the support. The modification of tail spacings to fit the actual spacing of the support can then be predicted along with the canting angle. With these starting structures we would carry out molecular mechanics and molecular dynamics calculations to obtain more accurate predictions of structure and properties (cohesive energy, vibrational frequencies, entropy, specific heat). This would be followed by experiments focusing on the best cases.

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