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SELF-ORGANIZATION OF LONG-CHAIN ALIPHATIC MOLECULES AND THEIR DERIVATIVES ON ATOMICALLY FLAT SURFACES

Using the scanning tunneling microscopy, it is found that the structural organization of n-alkane molecules n-C_nH_{2n+2} ($n = 10 \div 50$) on the reconstructed Au(111) surface varies non-monotonically, as the length of a molecule changes. The nonmonotonic character of the adsorption reveals itself in the alternation of packing types, dependence of the monolayer stability on n, and modification of surface properties. In the framework of the proposed one-dimensional model, it is shown that the correlation between the structure of adsorbed monolayers and the length of molecules is caused by a mismatch between the periods of the alkyl chain and the Au(111) surface along the $\langle 110 \rangle$ direction. The one-end functionalization of n-alkane molecules due to the chemically active –SH (n-alkanethiols) or –COOH (n-acids) group is demonstrated to result in the formation of a brush-like structure with " vertical" geometry of the adsorption, in which the anchoring of molecules at the surface occurs owing to the formation of covalent bonds.

K e y w o r d s: scanning tunneling microscopy, long-chain molecules of n-alkanes.

1. Introduction

Ultrathin organic films adsorbed on atomically smooth surfaces are a key subject in many experimental and theoretical researches. This circumstance is associated with their wide application in molecular electronics [1], in information displays [2], at the development of organic field-effect transistors [3], solar batteries [2], in pyroelectric detectors, and in other sensors [4]. Physical properties of such films depend on the degree of their ordering and, to a great extent, are determined by the first monolayer. Therefore, a special attention is given to the study of the factors that govern the structure of monolayers and their interaction with the substrate.

After the discovery of the scanning tunneling microscopy (STM) method in 1982, the observation of molecular structures with a spatial resolution that can reach, in some cases, a few hundreds of nanometers became possible. Historically, the first STM images with a molecular resolution were obtained in ultrahigh vacuum. However, the STM researches of organic films in vacuum are extremely laborious and expensive. Moreover, the vacuum STM systems are characterized by principal restrictions with respect to

a lot of organic adsorbates, in particular, to those that cannot be deposited on a substrate in vacuum owing to the thermal instability of molecules.

An alternative approach consists in the adaptation of STM to a liquid medium. In this case, organic films are deposited in a chemically inert solution, which plays the role of a tunnel medium and, simultaneously, protects the interface from the action of the atmosphere, i.e. it creates quasivacuum conditions for the substrate. This is an essentially important factor, when surfaces unstable in the atmosphere are used; in particular, it may be a reconstructed Au(111) surface, which is studied in this work.

Below, we report the results of our systematic STM researches on the adsorption of long-chain molecules of n-alkanes n-C_nH_{2n+2} ($n = 10 \div 50$) and some of their derivatives obtained by functionalizing the alkyl chain using the active –SH (n-alkanethiols) and –COOH (n-acids) groups. The reconstructed Au(111) surface is the main substrate to study in the present work. For the sake of comparison, some experiments were also carried out on highly oriented pyrolytic graphite.
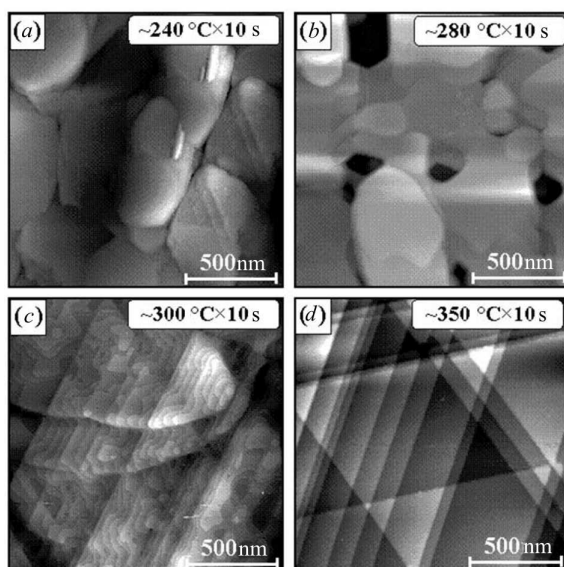
2. Experimental Part

Atomically smooth graphite substrates were fabricated by cleaving a commercial graphite single crys-
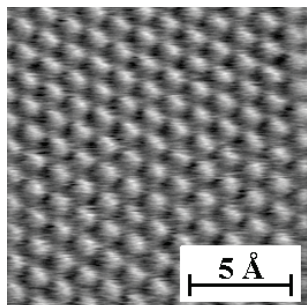
Fig. 1. STM image of the as-cleaved facet of a graphite single crystal with atomic resolution. Tunneling parameters: $I_t = 0.5$ nA, $U_t = 200$ mV

Fig. 2. Consecutive STM images of a gold film sputtered on a mica wafer depending on the annealing temperature (*a* to *d*). In panels *b* to *d*, the gradual formation of smooth atomic Au(111) terraces can be observed. Tunneling parameters: $I_t = 0.5$ nA, $U_t = 500$ mV

tal (Good Fellow). STM images revealed the atomic structure on the cleavage surfaces shown in Fig. 1.

For the fabrication of Au(111) substrates, single-crystalline mica wafers (United Mineral and Chemical Corp.) were used. Gold films (99.99%, Metron) 150 ± 50 nm in thickness were sputtered onto the as-cleaved surfaces of mica wafers. Sputtering was carried out at a rate of 0.2–0.3 nm/s in vacuum with a pressure of residual gases not higher than about 10^{-8} Pa. The substrate temperature was maintained within the interval of 500 ± 20 K and measured by

a thermocouple. The thicknesses of gold films were controlled by means of a silica balance.

The surfaces of Au substrates sputtered in such a way had a granular structure (Fig. 2, *a*). In order to form atomically smooth Au(111) terraces, the films were annealed under atmospheric conditions with the help of a gas-heated soldering iron (about 1–2 min before the deposition of solutions of the examined substances). Propane, butane, or their mixture taken in an arbitrary ratio were used as a working gas at the annealing. The annealing procedure consisted in the short-term (for about 10 s) insertion of the substrate into the flame region with a temperature of 650 ± 50 K. After the annealing, prolonged single-crystalline blocks with atomically smooth terraces separated by mono- or multiatomic steps were formed (Fig. 2, *d*). The terrace length reached several hundreds of nanometers. During the first 5–10 min after the annealing, the STM analysis revealed characteristic lines of the $23 \times \sqrt{3}$ reconstruction, which testified that the flat terraces are densely packed Au(111) facets.

For the deposition of films of *n*-alkanes, *n*-tetradecane n-$C_{14}H_{30}$ was used as a solvent, whereas, in the case of functionalized *n*-alkanes, it was methanol CH_3OH. The concentration and the volume of a solution per unit area of the substrate surface were experimentally selected so that a monolayer was formed on Au(111) after the complete deposition of a substance. The surface coverage was monitored with the use of STM images with subnanometer resolution.

STM measurements were carried out on a commercial STM device (NT MDT (Russia)), which was adapted by us to the liquid medium. The tips were fabricated by mechanically sharpening a Pt–Ir wire 0.25 mm in diameter. The film deposition and subsequent STM measurements were carried out at room temperature. STM images were obtained in the direct current regime without any filtration procedures, except for the subtraction of the average inclination of the scanning plane in order to improve the illustrative character of STM images.

3. Results and Their Discussion

3.1. Structure of n-alkane monolayers on graphite surface

We found that the molecules of *n*-alkanes, C_nH_{2n+2} (hereafter, C_n), with $n > 17$ form lamellar mono-

layers on the graphite surface, the structure of which does not depend on the length of molecules (the number n). The principal axes of molecules in lamellae are perpendicular to the lamella direction (Fig. 3). Spots with enhanced brightness in every molecule correspond to CH_2 groups of the alkyl chain. The attention is attracted by the fact that the number of light spots observed in the STM image equals half the number of carbon atoms in a molecule, which is explained by peculiarities in the substrate structure. The neighbor layers in graphite single crystals are known to be so relatively shifted that a half of carbon atoms in the first layer become arranged over the centers of carbon atoms located below (exhibited by white circles in the right panel of Fig. 3), and the other half over the centers of hexagons (gray circles). Hence, the graphite surface is represented by atoms of two types, conditionally, types α and β. Since the amplitudes of Z modulation of α and β atoms are substantially different, the STM contrast of a clean surface is formed by the atoms of only one type. In other words, every second atom on the graphite surface is invisible in the STM image. At the same time, the electronic contribution of substrate atoms to the STM contrast of adsorbed molecules can be considerable, and, in some case, it can dominate over the contribution by molecular orbitals. Therefore, the STM contrast of molecular fragments depends on their atomic environment, i.e. the types of carbon atoms near the fragment. When n-alkanes are adsorbed, the STM contrast of CH_2 groups located near the α-atoms is by an order of magnitude stronger (with respect to the amplitude of Z modulation) than that of the groups located near the β-ones. That is why the STM images (Fig. 3) demonstrate every second CH_2 group in the alkyl chain, whereas other CH_2 groups remain invisible as a result of their unfavorable atomic environment. The brightness variation of CH_2 groups along the axis of a C36 molecule originates from a mismatch between the periods of the alkyl chain and the substrate (0.251 and 0.246 nm, respectively).

3.2. Structure of n-alkane monolayers on Au(111) surface

The adsorption of n-alkanes on the reconstructed Au(111) surface is studied in the interval of numbers $n = 10 \div 50$, i.e. from n-decane (C10) to pentacontane (C50). We established that the adsorption
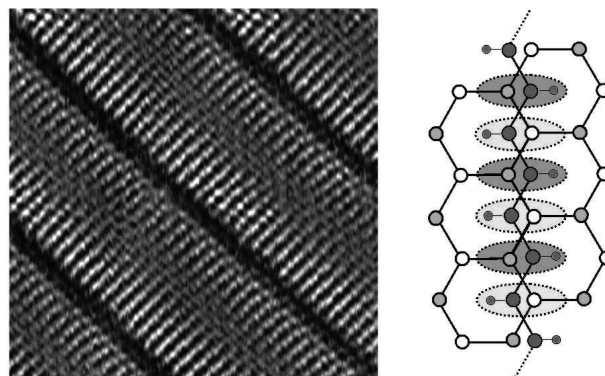
Fig. 3. (Left) STM image of the n-$C_{36}H_{74}$ monolayer on graphite. Tunneling parameters: 21×21 nm^2, $I_t = 0.1$ nA, $U_t = 100$ mV. (Right) Schematic model explaining the STM contrast enhancement for every second CH_2 group in the alkyl chain adsorbed on graphite (see the text)

behavior of n-alkanes on the Au(111) surface drastically differs from their adsorption on graphite. The first difference consists in the nonmonotonic variation of both stability and structure of monolayers. For instance, the ordering occurs in two number intervals: $10 \leqslant n < 16$ and $28 < n \leqslant 50$. At $18 \leqslant n \leqslant 26$, n-alkane films are disordered (the instability interval) (see Fig. 4). Another difference consists in that, under the same conditions, n-alkanes form structures of two types on the Au(111) surface: a stable structure with the perpendicular orientation of molecules relative to the direction of lamellae ($\alpha = 90° \pm 1°$, type A) and a metastable one with a tilted orientation ($\alpha = 60° \pm 1°$, type B). The packing of type A is observed for "magic" n values, which are multiple of 16 ($n = 16, 32, 48$), and the type-B packing for all other n in the examined length interval ($10 \leqslant n \leqslant 50$, $n \neq (16, 32, 48)$). Some examples of the packing for C48 and C36 molecules are depicted in Fig. 5.

The nonmonotonic character of the adsorption of n-alkanes on the Au(111) surface is explained by a mismatch between the periods of the alkyl link (0.251 nm) and the Au(111) substrate in the direction $\langle 110 \rangle$ (0.288 nm). By analyzing the intermolecular distances and the orientations of molecules with respect to the substrate, we found that the molecules of n-alkanes are adsorbed in every second groove on the Au(111) surface. This fact allows us to consider the behavior of n-alkanes in the framework of a one-dimensional model schematically shown in Fig. 6. Every adsorption groove in the model is a system of
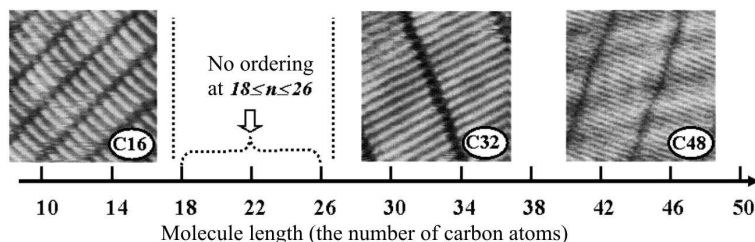
Fig. 4. Ordered structures observed in two intervals of n-numbers: $10 \leq n < 18$ and $26 < n \leq 50$. In the interval $18 \leq n \leq 26$, STM did not reveal any ordering
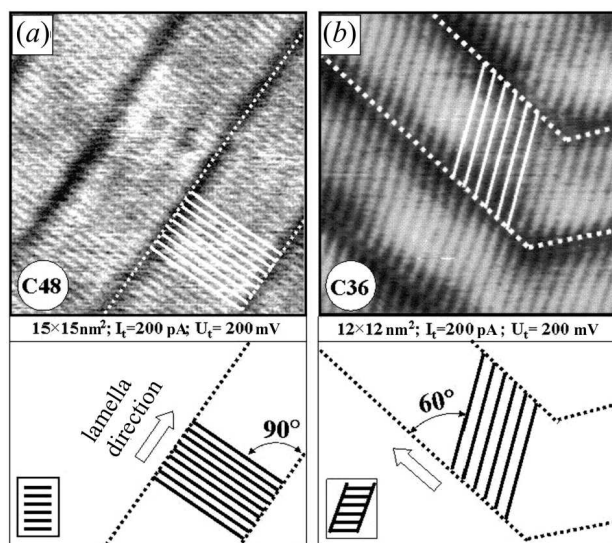

Fig. 5. Two types of the n-alkane packing on the Au(111) surface: (*a*) rectangular packing of n-octatetracontane C48, principal axes of molecules are perpendicular to the lamella direction; (*b*) slanting packing C36, molecules are slanted by about 60° with respect to the lamella direction

linearly located centers associated with a row of Au atoms oriented in the $\langle 110 \rangle$ direction.

Taking into account that the intramolecular STM image of n-alkanes shows only every second CH$_2$ group in the alkyl chains, let us idealize the adsorption geometry and consider the carbon atoms to be located in the plane perpendicular to the substrate. The interaction of the united centers of molecules with one another and with the centers of Au atoms forming the adsorption groove is described by the standard 6-12 Lennard-Jones potential,

$$U = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right],$$
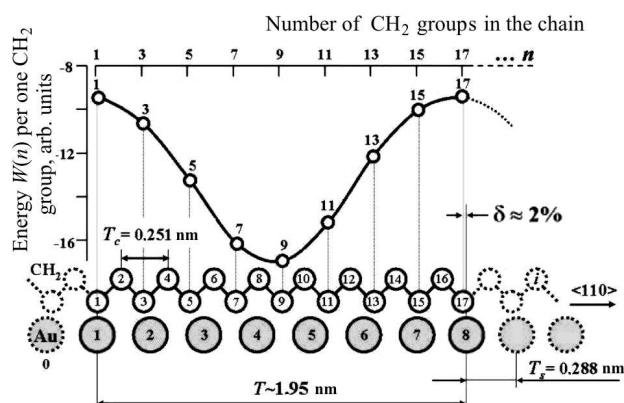
Fig. 6. One-dimensional model of adsorption of an infinite alkyl chain on the Au(111) surface. The adsorption groove is simulated by a chain of Au atoms. The scale along the $\langle 110 \rangle$ direction is preserved. The period of commensurability between the alkyl chain and the adsorption groove equals 1.95 nm with an error of about 2%. The periodic curve exhibits the energy of CH$_2$ groups as a function of the number n

where r_{ij} is the distance between the i-th and j-th centers. The values of ε and σ were put equal to 1.

In the framework of the described model, the calculations of the average interaction energy of CH$_2$ groups, $\langle W(n) \rangle$, as a function of the molecule length were carried out:

$$\langle W(n) \rangle = \frac{1}{n} \sum_{i=1}^{n} W_i,$$

where n is the number of carbon atoms in the alkyl link.

The generalized dependence $\langle W(n) \rangle$ is shown in Fig. 7. The attention is attracted by the nonmonotonic character of the curve $\langle W(n) \rangle$, which demonstrates a strongly pronounced maximum at $n = 22$. As one can see, near the maximum, the magnitude of

average interaction potential energy of CH$_2$ groups, $|\langle W(n)\rangle|$, has a minimum, which testifies to a weakening of the interaction between the molecules with the length close to that of C22. At the same time, $|\langle W(n)\rangle|$ grows, as n decreases, which evidences a strong coupling between the CH$_2$ groups of short alkanes. The horizontal dashed line in Fig. 7 cuts off the upper section of the curve $\langle W(n)\rangle$, which corresponds to the "instability interval" ($18 \leqslant n \leqslant 26$). Its position with respect to the curve $\langle W(n)\rangle$ is determined by the limits of "instability interval" (C18, C26) and corresponds to the experimental temperature ($T = 295 \pm 1$ K). The presence of "instability interval" for monolayers on the Au(111) surface is connected with the weakened adhesion of CH$_2$ groups in n-alkanes from C18 to C26, which is evident from the calculated curve $\langle W(n)\rangle$.

In the framework of the same model, we calculated the migration barrier for molecules along the $\langle 100\rangle$ direction. This parameter turned out anomalously low for n-alkanes with "magic" $n = 16, 32$, and 48. This means that, in the course of ordering, the molecules with the "magic" length move almost freely along the grooves and can form stable structures with rectangular packing. At the same time, the molecules with "non-magic" n form a metastable slanted packing. The model proposed not only explains the adsorption anomalies in the system n-alkane/Au(111), but also predicts a substantial decrease of friction for monolayers of alkanes with "magic" n, which was confirmed in our tribological experiments.

3.3. Structure of monolayers of functionalized n-alkanes

The structure of monolayers of functionalized n-alkanes was studied using octane acid (the functional group –COOH) and dodecanethiol (the group –SH), as examples. We also studied monolayers of molecules with the simultaneous double-ended functionalization using the –COOH and –SH groups (thiolated acids). When any of those three substances were deposited on the graphite surface, STM images did not revealed any manifestation of the ordering. Whereas, in the case of Au(111) substrate, the ordered structures with the vertical geometry of adsorption were found. Since the structure of monolayers of n-octane acid completely coincides with that for n-dodecanethiol, let us consider the results obtained for n-octane acid.


Molecule length (the number of carbon atoms)

$$\langle W(n)\rangle = \frac{1}{n}\sum_{i=1}^{n} W_i$$
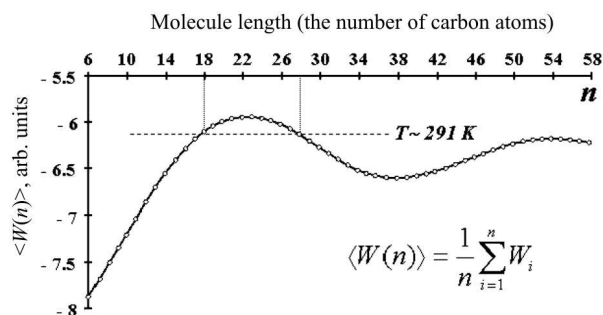
Fig. 7. Dependence of the average interaction energy $\langle W(n)\rangle$ of CH$_2$ groups of n-alkane molecules adsorbed on the Au(111) surface on the molecule length n. Calculations were carried out for even n in the interval $6 \leq n \leq 58$. The dashed line cuts off the instability section $18 \leq n \leq 26$


500×500 nm², I$_t$= 0,4 nA, U$_t$= 0,6 V
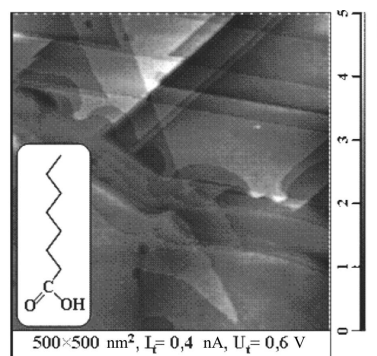
Fig. 8. STM image of a monolayer of n-octane acid CH$_3$-(CH$_2$)$_6$-COOH on the Au(111) surface on the submicron scale. The structural formula of n-octane acid is shown in the inset

The molecule of n-octane acid (see the inset in Fig. 8) consists of a linear hydrocarbonic chain about 0.9 nm in length and an end –COOH group. After depositing the corresponding solution, the STM images on the submicron scale revealed flat terraces several hundreds of nanometers in length on the Au(111) substrate. The characteristic lines of the $23 \times \sqrt{3}$ reconstruction of the Au(111) surface were reproduced in the STM before the solution deposition, but they were not observed after the film deposition. However, local current-voltage characteristics obtained before and after the solution deposition testified to the presence of a film on the substrate.

From the STM image obtained on the nanometer scale (Fig. 9, a), one can see that, in the presence of an acid film, the Au(111) terraces lose their atomic smoothness and become covered with a net-
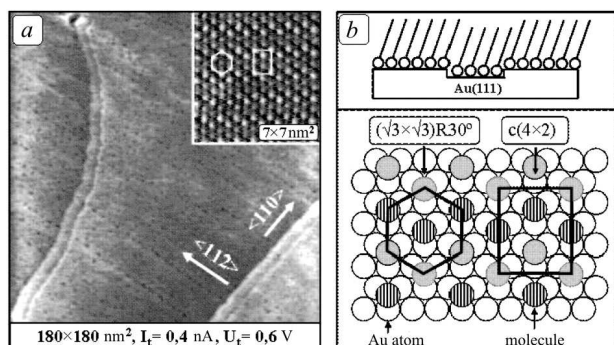
Fig. 9. (*a*) STM image of a monolayer of *n*-octane acid on the Au(111) surface on the nanomicron scale. Etched substrate sites testify to a chemical activity of COOH groups. The film image of a 7×7-nm^2 film section obtained with molecular resolution is shown in the inset. The hexagon and the rectangle mark the elementary packing cells of COOH groups and alkyl chains, respectively. (*b*) (Upper panel) Schematic model of the "brush-like" structure; (lower panel) schematic packing models of COOH groups (the structure $(\sqrt{3} \times \sqrt{3})R30°$) and alkyl chains (the superstructure $c(4 \times 2)$). Gray and hatched circles denote alkyl chains with different environments
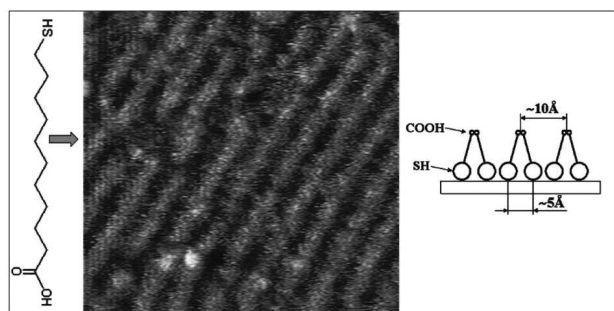
Fig. 10. (Left panel) STM image of a monolayer of thiolated *n*-dodecane acid on the Au(111) surface. A row structure with doubled period is observed. Scanning parameters: 10×10 nm^2, $I_t = 0.5$ nA, $U_t = 500$ mV. (Right panel) Schematic explanation of the packing structure. The doubled period results from the association of COOH groups of molecules in neighbor rows

work of dips that look like dark spots (the so-called "leopard" structure [5]). The analysis of STM images showed that all spots have an approximately identical depth equal to the height of a monoatomic gold step (about 2.4 Å). Hence, the dips are vacancies in both the first layer of the Au(111) substrate and the "leopard" structures of *n*-alkanethiols [6]. By analogy with thiols, the presence of the "leopard" structure in the films of *n*-octane acid testifies to the chemical activ-

ity of its molecules with respect to the reconstructed Au(111) surface.

The STM image with molecular-level resolution (see the inset in Fig. 9, *a*) demonstrates a regular arrangement of spots with a varying brightness. The distance between neighbor spots equals 0.5 ± 0.02 nm, which agrees well with the diameter of a head COOH group. Hence, the observed spots correspond to separate acid molecules. The fact attracts attention that the monolayer packing is a superposition of two elementary cells with different symmetries: hexagonal (independent of the spot brightness) and rectangular, which corresponds to the arrangement of spots with the enhanced brightness (see the inset in Fig. 9, *a*). We may suppose that the molecules become adsorbed into linear conformations so that their principal axes are tilted with respect to the Au(111) surface (see the inset in Fig. 9, *b*). In so doing, their end –COOH groups contact with the substrate, and the alkyl chains are directed to the liquid (the so-called "brush-like" structure with the vertical adsorption geometry). The distance between the neighbor molecules (0.5 ± 0.02 nm) determined from the STM image (Fig. 9, *a*) is close to $\sqrt{3}a = 0.498$ nm, where $a = 0.288$ nm is the lattice period on the Au(111) surface. This distance coincides with that between the $\langle 110 \rangle$ rows of gold atoms. Taking those distances into account and proceeding from the fact that the long-period modulations of the STM contrast were never observed while scanning the flat monolayer sections, we may assert that the film is commensurate with the Au (111) substrate along three equivalent directions $\langle 112 \rangle$, $\langle 121 \rangle$, and $\langle 211 \rangle$.

The presence of two structures can be explained by the packing difference between the head parts of molecules (COOH groups) and alkyl chains. We consider that, in the monolayer, the COOH groups of all molecules occupy equivalent adsorption sites and form a hexagonal $(\sqrt{3} \times \sqrt{3})R30°$ structure with the basis vectors $a = b = 0.5 \pm 0.02$ nm. In this case, the packing of alkyl chains corresponds to a rectangular structure $c(4 \times 2)$. Within a unit $c(4 \times 2)$ cell, the environments of alkyl chains are nonequivalent, which is responsible for the difference between their STM contrasts. A schematic packing model for the molecules of *n*-octane acid is depicted in Fig. 9, *b*. However, it should be noted that the molecules can occupy adsorption sites of three types on the Au(111) surface: hollows located amid three nearest atoms ("three-fold

hollow" sites), tops of gold atoms ("top" sites), and "bridge" sites [7]. It is evident that, in each of those cases, the packing structure is determined by the same basis vectors of the lattice. In the model proposed in Fig. 9, *b*, the molecules occupy bridge positions. Unfortunately, since it was impossible to visualize the atomic structure of the substrate, we did not manage to determine the type of adsorption sites.

When the deposition is carried out from a liquid, it is known that the solvent type can substantially affect the structure and the properties of the obtained films [8]. In order to elucidate this circumstance, we carried out experiments with two solvents with different polarities: polar methanol CH_3OH and non-polar *n*-tetradecane n-$C_{14}H_{30}$. The monolayer structure of *n*-octane acid turned out independent of the solvent type. Moreover, the film structure described above was observed both in the fluid environment and after the complete solvent evaporation. Hence, the deposition technique used in this work can form a basis for the technology of fabrication of the "dry" monolayers of saturated organic acids.

At last, we studied the adsorption of molecules with the two-end functionalization by –SH and –COOH groups (thiolated *n*-dodecane acid). The STM image of its monolayer is shown in the left panel of Fig. 10. Unlike the monolayers of *n*-acids and *n*-alkanethiols, in which the distance between the molecular rows amounts to about 5 Å, a doubled distance between the neighbor rows (about 10 Å) is observed in this case. This fact can be explained by the association of COOH groups in the monolayer (the relevant schematic explanation is shown in the right panel of Fig. 10).

4. Conclusions

With the help of STM, it is found that the structural organization of *n*-alkanes (n-C_nH_{2n+2}) on the reconstructed Au(111) surface changes nonmonotonically, as the chain length varies, which manifests itself in the alternation of packing types and in the dependence of the monolayer stability on n. For the explanation of adsorption anomalies in the system *n*-alkane/Au(111), a one-dimensional model is proposed, the key parameter of which is the commensurability between the alkyl link length and the period of the substrate lattice. In the framework of the model, the correlation between the structure of adsorbed monolayers and the length of molecules is shown to follow from the difference between the periods of alkyl links and the Au(111) substrate in the $\langle 110 \rangle$ direction. The functionalization of *n*-alkane molecules with –SH and –COOH groups gives rise to the formation of "brush-like" structures with the vertical adsorption geometry.

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САМООРГАНІЗАЦІЯ
ДОВГОЛАНЦЮЖКОВИХ АЛІФАТИЧНИХ
МОЛЕКУЛ ТА ЇХ ПОХІДНИХ НА АТОМНО
ГЛАДКИХ ПОВЕРХНЯХ

Р е з ю м е

За допомогою методу сканувальної тунельної мікроскопії (СТМ) встановлено, що характер структурної організації *n*-алканів n-C_nH_{2n+2} ($n = 10–50$) на реконструйованій поверхні Au(111) змінюється немонотонно з довжиною молекули. Немонотонний характер адсорбції проявляється в чергуванні типів пакувань, у залежності стабільності моношарів від n, а також у зміні їх поверхневих властивостей. У рамках запропонованої одновимірної моделі показано, що кореляція між структурою адсорбованих моношарів і довжиною молекул зумовлена неузгодженістю періодів алкільного ланцюга і поверхні Au(111) у напрямку $\langle 110 \rangle$. Продемонстровано, що одностороння функціоналізація молекул *n*-алканів хімічно активними групами –SH (*n*-алкантіоли), –COOH (*n*-кислоти) приводить до формування щіткоподібних структур з "вертикальною" геометрією адсорбції, в яких зв'язок молекул з поверхнею здійснюється за рахунок ковалентної взаємодії.