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Self-organization of monodentate organic molecules on a solid surface — A Monte Carlo and transfer-matrix study

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ABSTRACT

A lattice gas model of monodentate organic molecules on a solid surface in terms of pair directional interactions has been developed. As a special case of the constructed model the self-organization of CaTBPP on Au(111) surface was studied with Monte Carlo and transfer-matrix methods in the grand canonical ensemble. It is shown that the adsorbed molecules tend to form dimers when the hydrogen bonding between the molecules is relatively strong. Phase behavior of the system in this case can be characterized as the hierarchical self-assembly process. The self-assembly is led by the repulsive interactions between the building blocks those are the dimers of the adsorbate molecules stabilized with the strong hydrogen bonding. When hydrogen bonding is weak, a cross-like structure appears at moderate surface coverages.

1. Introduction

Supramolecular self-assembly of organic molecules on a solid surface is one of the most effective approaches to creating functional nanostructures. However, a detailed understanding of mechanisms and regularities of the basic physicochemical processes in the adsorption overlayers is required to control the self-assembly process.

Such nanosystems have a huge potential for practical applications. Some of them have already been successfully used as molecular electronic logic elements in the various storage devices [1–4], photocurrent generation [5], active elements of gas sensors [6] etc. Self-structured adsorption layers of some alkanethiols on the gold and silver surfaces are used to study the interaction of synthetic materials with biological systems [7].

The main factors affecting the formation and stability of organic adsorption monolayers are: 1) complicated adsorbate–adsorbent interactions, resulting in the possibility of different orientations of the molecules with respect to the surface and, therefore, several types of adsorption complexes depending on the external conditions (temperature, pressure, electrode potential etc.) [8–17]; 2) specific interactions between adsorbed molecules [18–26].

Recently, it was shown that the complicated interactions with metal surfaces can be described by the lattice gas models those that take into account the multisite character of adsorption process. The simplest model of this type is the model of dimer adsorption that allows for the vertical and horizontal orientation of the molecule with respect to the surface [8–10].

Nature of interactions between the adsorbed molecules may be different. In most cases it is non-covalent interaction, such as Van der Waals force, dipole–dipole interaction, indirect interaction through the substrate and hydrogen bonding [2,27,28]. One of the major criteria is stability of the adsorbed monolayer. From this point of view, the strongest and directed interactions such as metal-ligand coordination and hydrogen bonding are the most preferable to create the stable self-assembled nanostructures. In this paper, the main attention is paid to the hydrogen bonds. It usually occurs between the functional groups which are composed of covalently associated electronegative and hydrogen atoms. Due to the tendency of hydrogen atom to become positively polarized and their small size, they can strongly interact with nearby electronegative atoms. This interaction leads to the formation of hydrogen "bridge" — a connection, where the hydrogen acts as an intermediary between two electronegative atoms. As a consequence, the hydrogen bond is relatively stable and has a directional character. Typically, its value ranging from 8 to 40 kJ/mol, but in exceptional cases can reach very high values. This contributes substantially to the formation of complex molecular architectures with different symmetries.

It was shown that the phase behavior of the adsorbed systems under consideration can be described by the single site lattice gas model with directional interactions. An example is the model of trimesic acid (TMA) adsorption on a triangular lattice [18–20]. It is worth to note that there is the "devil's staircase" of phase transitions in this simple model [19]. It

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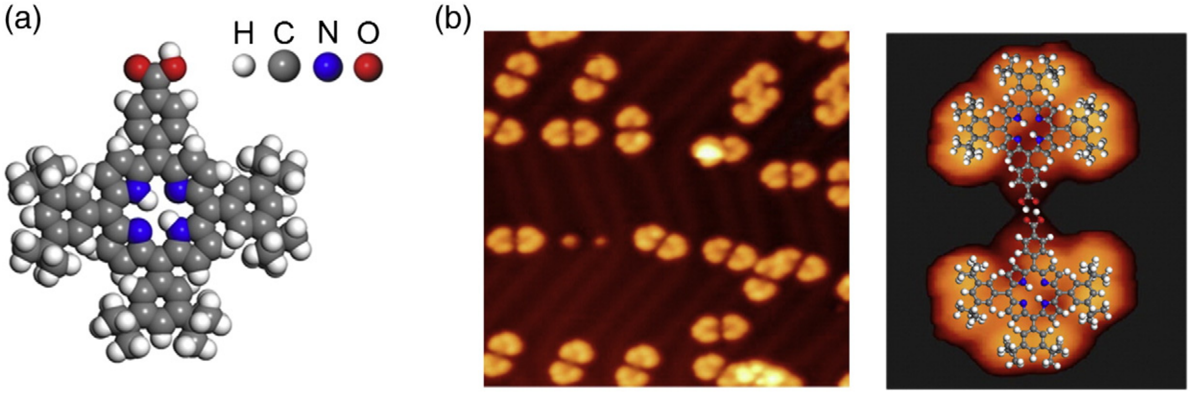

Fig. 1. (a) Chemical structure of CaTBPP molecule and (b) STM images of CaTBPP molecules on Au(111) surface [29] and model of CaTBPP dimer.

occurs as the result of the competing pair and trimeric directional interactions.

The adsorption model of TMA demonstrates a significant impact of the directional interactions on the phase behavior of the adsorption monolayer. Triangular symmetry in the arrangement of the functional groups allows one to consider the adsorption monolayer of TMA as a model system to study general regularities of the formation of continuous 2D ensembles stabilized by hydrogen bonds on the solid surface. In this paper, we study the general case of adsorption of large monodentate organic molecules on a solid surface. As a special case of the model we investigate 5-(4-carboxyphenyl)-10, 15, 20-tri (3, 5-di-t-butylphenyl) porphyrin (CaTBPP) adsorption (Fig. 1) on Au(111) surface [29,30]. According to the general considerations [22], monodentate organic molecules such as CaTBPP and molecules with a similar chemical structure are capable to form the discrete dimer-like molecular ensembles on solid surfaces. Unlike TMA molecule, the CaTBPP molecule has the square symmetry and only one functional group to form the hydrogen bond. It suggests high interaction anisotropy in the adsorption overlayer.

STM snapshot of the Au(111) surface at 63 K after a small deposition of the CaTBPP obtained by Yokoyama et al. [29] is shown in the Fig. 1b. It is seen that the dimer-like structures are mainly formed on the surface. It occurs due to the hydrogen bonding between two adsorbed molecules.

In this paper, the lattice gas model was used to study the thermodynamic regularities of the self-organization of CaTBPP adlayer and its phase behavior. The molecule has a rather complex structure. Therefore, we have to adopt the following assumptions:

1) CaTBPP molecule is large and physically adsorbs onto several tens of atoms. In this regard, the molecule is located quite freely on the solid surface without being tied to any specific active sites. This is clearly seen in Fig. 1. The symmetry of the lattice in our model was chosen based on the geometry of the most favorable pair interactions, the symmetry and chemical structure of the molecule. Namely, a square lattice consisted of $M = L \times L$ adsorption sites was chosen as a surface model. One site is defined as a group of atoms occupied by a single molecule.
2) In this paper, we focus on the study of directional interactions between the molecules in the adsorbed monolayer. As it is demonstrated below, considering only pairwise directional interactions between the adsorbed molecules allows us to take into account the hydrogen bonding between adsorbed molecules (attractive interactions), own size effects and chemical structure of the molecule (repulsive interactions) in the framework of the relatively simple lattice gas model.
3) Due to a relative inertness of Au(111) surface, the planar adsorption structure is the most energetically favorable configuration of the CaTBPP molecule on the surface. It is the consequence of the van der Waals interactions between gold atoms and atoms of CaTBPP molecule. Therefore, we do not consider the possibility of different orientations of the molecule with respect to the solid surface. Without any loss of generality, we can assume that one molecule occupies only one adsorption site with adsorption energy equaled to zero.

Thus, in this study the lattice gas model of single site adsorption, wherein each adsorbed molecule has one preferential direction due to the presence of one functional group (Fig. 2a) was developed. The model is implemented to describe the adsorption monolayer of the monodentate CaTBPP organic molecules and molecules with a similar chemical structure.

The adsorbate molecules within the framework of the proposed model can be oriented on the surface in four different ways (Fig. 2a). Taking into account the possibility of empty site, a total number of the possible states of the lattice site equals to 5. Note that the special case of our model is similar to the special one of the well-known Potts model [31] with $q = 5$. The main difference is the directional character of the interactions in the proposed model. The energies of such interactions depend on the relative positions and orientations of the molecules. Thus, there are ten different pair configurations of the adsorbed molecules (Fig. 2b). In order to minimize the amount of model parameters, we make some assumptions: the pair configuration, where molecules arrange a functional group (carboxyphenyl) to each other, has the energy w_1; the energy of adsorption configuration, where molecules arrange

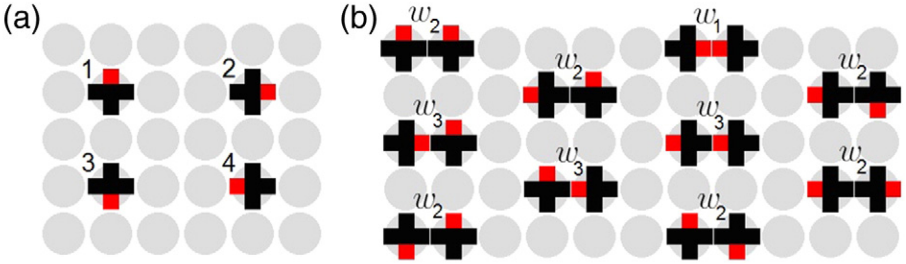

Fig. 2. (a) Possible arrangements of the molecules on square lattice and (b) possible pair configurations with the corresponding interaction energies.