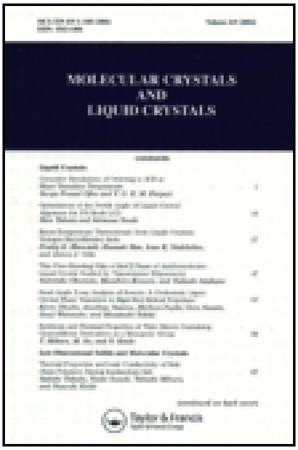

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Molecular Arrangement in Peptide Self-Assembled Monolayer on Metallic Surface

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Molecular Arrangement in Peptide Self-Assembled Monolayer on Metallic Surface

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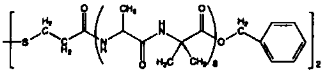
We numerically investigate the molecular arrangement and orientation in the self-assembled peptide monolayer adsorbed on metal surface in terms of intermolecular dipole-dipole interaction. Based on a model considering the distribution of dipoles in a molecule, we obtain stable and meta-stable orientations in two crystalline molecular arrangements.

Keywords: self-assembled monolayer; dipole-dipole interaction; molecular arrangement; molecular orientation

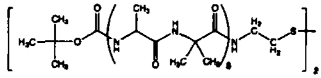
INTRODUCTION

Investigation of molecular arrangement, especially in a self-assembled monolayer (SAM)[1], is important in the technology for functional organic thin films in terms of design and control of their structure. Organosulfer helical peptides,



Peptide I

and



Peptide II,

are adsorbed on gold surface to form a SAM[2]. They possess molecular dipole moments of 55 D[3] which are in opposite sense to each other on the gold surface. It is thought that such large dipole moments provide significant dipole-dipole interactions playing an important role in the molecular arrangement. Experimentally, it is reported that a monolayer of equimolar mixture of these peptides shows larger thickness than that composed of one peptide, probably because antiparallel arrangement of these dipoles results in a stable high-density packing[2]. In this paper, we numerically discuss molecular arrangement of the self-assembled monolayer with a model considering the distribution of dipoles in a molecule.

MODEL

In Peptides I and II, 16 amide groups predominantly contribute to the molecular dipole. The amide groups are placed periodically on the helix of 25.7 Å long [4], while the intermolecular separation is 9.98 Å [2]. In order to take the distribution of dipoles into account, we employ the multiple dipole model in which we approximate the molecular dipole to 16 dipoles of 3.4 D (= 55 D/16) placed at the position of amides, as shown in Figure 1. This model is more plausible than the single dipole model in which molecular dipole is approximated to single point one at the center of gravity, because in the latter model there is a possibility to overestimate the intermolecular dipole-dipole interaction and to underestimate electrostatic potential of a molecule from the metal.

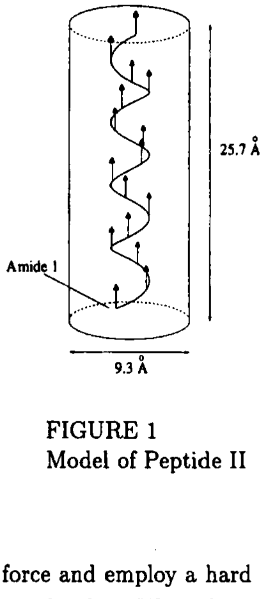


FIGURE 1
Model of Peptide II

In the calculation, we neglect the dispersion force and employ a hard core potential in order to avoid overlap between molecules. We include dipole-dipole interaction between molecules separated by less than the cutoff distance of 9.98Å×16. We introduce an electrostatic potential by the metal as a dipole-dipole interaction between the dipoles and their images.

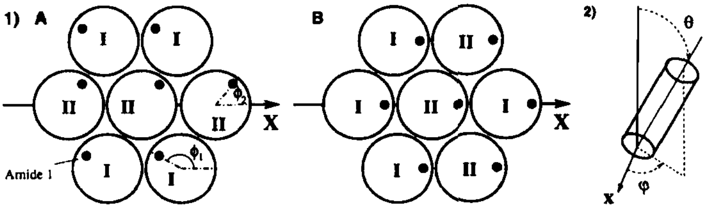


FIGURE 2 1) Two molecular arrangements for equimolar crystals. 2) Definition of tilt angle.

We suppose here that this SAM is a crystal with hexagonal two-dimensional lattice. There are two kinds of molecular arrangement in this SAM as shown in Figure 2. In this figure, I and II stands for peptide I and II, respectively. We assume that all molecules have the same tilt angle represented by (θ, φ) in spherical polar coordinates as shown in Figure 2-2). Rotation of the molecules around the molecular longitudinal axis is represented by the angle ϕ from the $+x$-axis to the amide group which is the nearest to the binding site for adsorption (Amide 1). For example, in Figure 2-1) B all of the Amide 1 is on the $+x$-axis and $\phi_1 = \phi_2 = 0$

RESULTS AND DISCUSSION

First, we calculate $(\theta,\ \varphi)$ dependence of the energy per one molecule. In molecular arrangement A and at $\phi_1 = \phi_2 = 0$, the minimum energy is obtained at $(\theta, \varphi) = (24.4°, 30°)$. $\theta = 24.4°$ is the maximum tilt without molecular overlapping at $\varphi = 30°$, 90° and 150°.

Next, we calculate the minimum energy and the tilt angle for it at various rotation angles $\phi (= \phi_1 = \phi_2)$ *. Figure 3 shows the obtained minimum energy as a function of ϕ in molecular arrangements A and B. In the arrangement A, the minimum energy is obtained at tilts of $(\theta, \varphi) = (24.4°, 30°)$ in $0 < \phi < 60°$ and $(24.4°, 90°)$ in $60° < \phi$ which are shown by arrows in Figure 3-1). The minimum energy becomes lowest at $\phi \sim 30°$ and 90°, and we can see 90° is more stable orientation in this arrangement.

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*We have verified that the system energy becomes the lowest when $\phi_1 = \phi_2$ in both arrangements by preliminary numerical experiments.

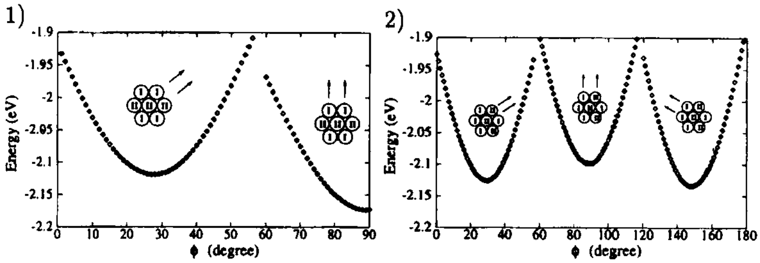

FIGURE 3 ϕ dependence of minimum energy per one molecule in molecular arrangements A and B.

In molecular arrangement B, the minimum energy is obtained at $(\theta, \varphi) = (24.4°, 30°)$ in $0 < \phi < 60°$, $(24.4°, 90°)$ in $60° < \phi < 120°$ and $(24.4°, 150°)$ in $120° < \phi < 180°$ as shown in Figure 3-2). The minimum energy becomes the lowest at $\phi \sim 30°, 90°$ and $150°$, and the most stable orientation is at $\phi = 150°$.

Comparing these two arrangements, we can see that the orientation $(\phi, \theta, \varphi) = (90°, 24.4°, 90°)$ in the arrangement A is the most stable. Thickness of the monolayer at this orientation is about 24 Å, consistent with experimental results.

Acknowledgments

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References

[1] A. Ulman, *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly* (Academic Press, San Diego, 1991), Part 3.

[2] K. Fujita, N. Bunjes, K. Nakajima, M. Hara, H. Sasabe and W. Knoll, *Langmuir,* **14,** 6167 (1998).

[3] A. Wada, *Adv. Biophys.*, **9**, 1 (1976).

[4] K. Otoda, Y. Kitagawa. S. Kimura and Y. Imanishi, *Biopolymers,* **33,** 1337 (1993).