

Dynamic Effects on Adsorption of Organic Molecules at Insulating Surfaces

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We present the results demonstrating the importance of entropic effects for adsorption, diffusion and interaction of flexible molecules with surface steps. Previous studies have mainly emphasized the enthalpy of adsorption and the interaction between molecules.^[1] Recent theoretical studies of the adsorption of individual flexible and rigid molecules on the KCl (001) surface have shown significant entropy loss during adsorption^[2]. Here we used NC-AFM and modelling to study the behaviour of 1,3,5-tri-(4-cyano-4,4 biphenyl)-benzene (TCB) and 1,4-bis(cyanophenyl)-2,5-bis(decyloxy)-benzene (CDB) molecules on KCl(001). Both molecules were designed to contain the same anchoring groups and benzene ring structures, yet differ in flexibility. They were deposited on the KCl (001) surface, and imaged using NC-AFM^[1]. CDB self-assembled structures were observed to grow from step edges, while TCB self-assembled structures grew as islands on the terrace and from step edges. Density functional theory (DFT) and molecular dynamics simulations were performed to explain the reasons behind this qualitative difference in growth character and how molecular flexibility can affect the diffusion of the molecules towards and along steps.

Lowest energy adsorption geometries of single molecules on a clean terrace were calculated using the van der Waals corrected DFT and the results were used to parameterise a force field for interaction of each molecule with KCl(001) employing a genetic algorithm^[3]. These force fields were then used to calculate diffusion coefficients and barriers for CDB and TCB on clean terraces. The flexible CDB molecule exhibits faster diffusion than the more rigid TCB molecule, which affects the film growth mechanisms of these molecules. Potential of mean force calculations were used to calculate the adsorption free energy for both molecules. It was found that entropic contributions are significant and can match the enthalpic contribution to adsorption energy at temperatures as low as 400K, thus facilitating desorption. Furthermore molecular diffusion towards and adhesion to step edges was investigated and the associated change in entropy was calculated. The results demonstrate that the conformational flexibility of the CDB molecule allows it to interact strongly with steps and kinks, where nucleation and subsequently cluster growth occurs. In contrast, the rigid TCB molecule is unable to adapt to step edges and kinks with a significant entropy loss upon adhesion on step edges. This difference in growth modes confirms experimental NC-AFM observations of different modes of layer growth.

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