Supramolecular effects of chiral molecules on metallic surfaces: D-alaninol on Cu(100) as a case study

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Organic chiral molecules adsorbed on metallic surfaces provide a simple and flexible way to transfer chirality to achiral substrates. The beneficial quality of the resulting structures ranges from their practical use as stereospecific catalysts or as substrates for possible homochiral propagation to supramolecular gratings. Many works have been devoted to the adsorption of amino acids on metallic surfaces [1]. We address here instead the adsorption of a simple amino alcohol, alaninol (2-amino-1-propanol), on Cu(100) as a case study. The molecule's bifunctional nature permits a possible double interaction taking place between both amino and hydroxyl groups on one side and copper atoms on the other. Among the two functional groups, the amino group is the one that is most strongly involved in the binding with the surface, making the hydroxyl group more easily available to create lateral hydrogen-bonded interactions with other molecules of the same type in a possible self-assembled surface structure. In this respect, chirality plays an additional role in permitting the creation of clusters of molecules at the surface with complex relationships occurring between them, instead of a simple molecular packing.

In order to investigate and possibly to enhance the achievable enantioselectivity, it is of primary importance to understand the mechanisms of adsorption at the surface. The practical use of such modified surfaces is made possible by the fact that a long-range ordered self-assembled molecular phase is formed upon adsorption. Experimentally [2], alaninol is found to self-assemble on Cu(100) forming, at monolayer coverage, a phase composed by tetrameric units. In particular, as shown by low energy electron diffraction (LEED), its D-enantiomer arranges in a square structure represented in matricial form as (1,4|4,-1) leading to a 14 degrees clockwise rotation of the molecular phase with respect to the [011] direction of copper. The tetramers composing this phase are presumably due to four alaninol molecules [3], that appear not exactly equal when imaged by a scanning tunnelling microscope (STM, see Fig. 1a). A complex interaction among molecules and between molecules and surface is therefore to be expected and a mere systematic search of all possible combinations of four molecules can be not sufficient to devise the type of molecular structure describing the system. In this work we therefore address the problem employing a composite approach based on the interplay betwen density functional theory (DFT) calculations and classical molecular dynamics. DFT is employed for providing the starting point, *i.e.* the adsorption configurations of a single alaninol molecule on the Cu(100) surface [4]. This shows that the most stable adsorption geometry involves the amino group and a less strong interaction with the surface through the hydroxyl group (see Fig. 1b). A tetramer of alaninol molecules is then assumed as initial configuration to start molecular dynamics at room temperature, in which N-Cu bonds are fixed, whereas the hydroxyl end of the molecules are left free to rotate on the surface. The successive dynamics is carried on for a few tens of nanoseconds, which allows the exploration of a good portion of the configuration space. Two different situations are addressed in the simulations: a first case in which the dynamics of a single tetramer is analyzed and a second case in which nine tetramers on a square matrix are considered. This two step approach allows to assess the comparative

importance of intra- and inter-tetramer forces. One of the outcomes of such calculations is that it is essential to take into account the larger simulation cell, that best matches the experimental situation, and that quite different results are obtained when comparing the most sampled geometries in the two cases. This points to the important role of supramolecular interactions and highlights the cooperative effect that takes place, correlating even molecules that are located several angstrom apart, as is shown by performing an essential dynamics analysis [5].
As a final point, we resort again to DFT calculations applied to the central tetramer of the most sampled geometries, simulating STM images and comparing them with available experimental data.

References:

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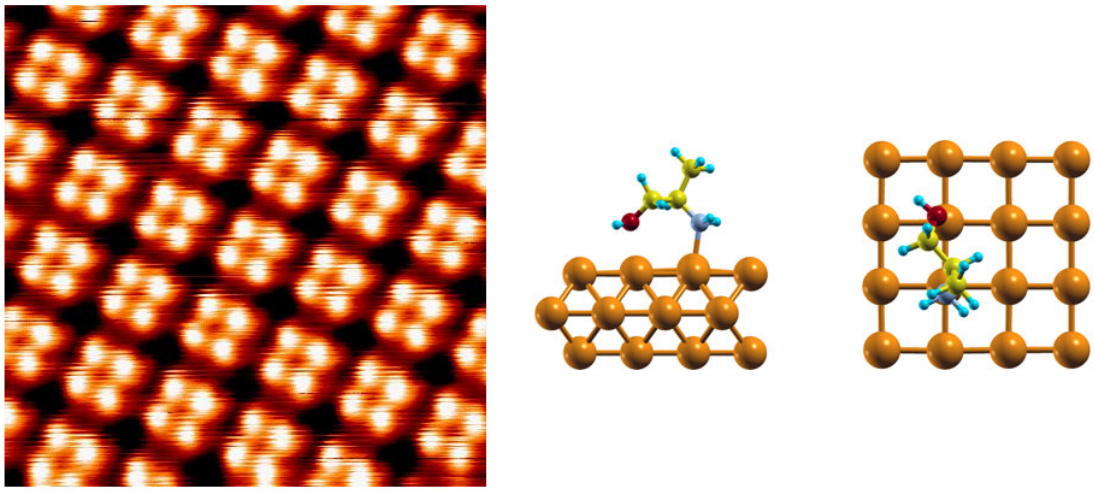
Figure 1



a) Experimental STM image of a 6 × 6 nm^2 area (V = 0.1 V; I = 0.2 nA); b) Most stable adsorption configuration (side and top view) of a single D-alaninol molecule adsorbed on Cu(100).