

Manipulation of covalently bound molecules with STM and AFM: a comparative theoretical study

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Controlled manipulation of atoms and molecules is the route to the assembly of complex molecular and atomic patterns in nanotechnology. Scanning tunnelling microscopy (STM) has been widely used to manipulate atoms and molecules laterally across the surface; vertical manipulation of atoms and small molecules has been achieved as well. An important feature of STM is that a bias voltage is applied to the surface, which is likely to disrupt the adsorbate-surface bonding and assist manipulation, but may also damage large complex molecules. In contrast, atomic force microscopy (AFM) manipulation relies solely on interatomic interactions. Vertical manipulation of atoms has been achieved by AFM. Manipulation of molecules with AFM, however, has not been thoroughly studied either experimentally or theoretically.

In this paper, we present the results of our theoretical modelling of manipulation of a large molecule, the C₆₀ fullerene, covalently bound to the Si(001) surface. We first discuss its vertical manipulation and demonstrate using density-functional theory (DFT) calculations the possibility of lifting this molecule from the surface due to the tip-molecule chemical interaction only, without applying bias voltage. To achieve a vertical manipulation, the molecule needs to be brought to a precursor state where its bonding to the surface is minimised. This type of manipulation is possible in STM but not in AFM, where the cantilever oscillation period is much longer than atomic relaxation times, and the molecule would relax from the metastable precursor state to a stable site.

Thus, manipulation of molecules due to tip-molecule chemical bonding is not likely to operate in AFM. However, a different mechanism can be employed: the lowering of a manipulation barrier due to the tip-molecule interaction. We explore the values of the C₆₀ manipulation barrier for various tip positions. We perform kinetic Monte Carlo simulations to determine the probabilities of the molecule jumping to a new adsorption site as a result of its interaction with an oscillating AFM tip. The potential energy surface calculated using DFT is fed into the virtual AFM code to study the actual response of the dynamic mode AFM apparatus to the successful manipulation of the fullerene molecule.