

C₆₀ Adsorption and Manipulation on the Si(001) Surface: A Theoretical Study

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Controlled manipulation of adsorbates on crystal surfaces is a promising process that can lead to assembly of clusters or nanolayers on crystal surfaces. In particular, manipulation of C₆₀ on the Si(001) surface -- the system characterised by strong covalent bonds between the surface and the adsorbate -- has been performed experimentally using the tip of a scanning tunnelling microscope (STM) [1]. However, the atomic-scale mechanism of the manipulation process, and particularly the role of bond breaking, is not yet well understood.

It is believed that atomistic processes during the manipulation events are not directly affected by the STM current that is used merely to control the tip position. Instead, these processes are caused by mutual interactions between the molecule, surface and the tip. Therefore, studying theoretically the mechanisms of STM assisted manipulation should help us in understanding general manipulation mechanisms that must be at work during future manipulation experiments to be performed using Atomic Force Microscopy (AFM).

We report the results of our theoretical modelling of adsorption and manipulation of C₆₀ on the 2x1-reconstructed Si(001) surface. The calculations were done using the density-functional code SIESTA within the generalised gradient approximation.

A variety of stable and metastable adsorption sites for the C₆₀ molecule on Si(001) was identified in our work [2] and in a previous study by Godwin et al. [3]. Diffusion of the molecule on silicon has been modelled using a simple constrained minimisation technique. We consider probable diffusion trajectories that may be initiated by the tip either pushing (repulsive mode) or pulling (attractive mode) the molecule. A number of different possible trajectories are studied including those along and across the through and the dimer row of the Si (001) surface. Several orientations and relative positions of the tip with respect to the molecule are also investigated.

Our calculations showed that the molecule goes through several different stable adsorption sites in which molecule is bound to four Si atoms on the surface. Transitions between stable sites occur according to a pivoting mechanism: in the transition state there are two bonds between the molecule and the surface, these act as a pivot over which the molecule rolls.

Thus, our calculations elucidate the complex mechanism of C₆₀ motion on the Si(001) surface and underscore the role of bonding and bond breaking in the process of surface diffusion of covalently bound adsorbates.

1. D.L. Keeling, M.J. Humphry, R.H.J. Fawcett, P.H. Beton, C. Hobbs and L. Kantorovich, *Phys. Rev. Lett.* 94 146104 (2005).

2. C. Hobbs, L. Kantorovich, J. Gale, submitted to *Surf. Sci.*

3. P.D. Godwin, S.D. Kenny and R. Smith, *Surf. Sci.* 529 237 (2003).