MANIPULATION ON THE 1 – 10NM SCALE USING LOCALISED FORCES AND EXCITATIONS: PROGRESS IN THE EU STRP NANOMAN*

We report progress in the EU funded NanoMan STRP which has as its focus the manipulation of molecules and nanoparticles using an atomic force microscope. The scope of this activity covers the construction of new instruments, controlled manipulation/modification on insulating, semiconductor and metallic surfaces using cantilever and tuning fork AFM probes and the development of theoretical models of the nanoscale processes relevant to manipulation using both AFM and STM.

In the talk we will describe the following:

Molecular switching on the Si(100) surface
The demonstration of the action of a molecular switch made of a biphenyl molecule adsorbed on a Si(100) surface has been achieved by the Orsay partner (Lastapis et.al. *Science* **308** 1000 (2005)). Tunneling electrons from a low temperature (5 Kelvin) scanning tunneling microscope (STM) were used to control, through resonant electronic excitation, the molecular dynamics of an individual biphenyl molecule adsorbed on a Si(100) surface. Different reversible molecular movements were selectively activated by tuning the electron energy and by selecting precise locations for the excitation inside the molecule. Both the spatial selectivity and energy dependence of the electronic control are supported by spectroscopic measurements with the STM. These experiments demonstrate the feasibility of controlling the molecular dynamics of a single molecule through the localization of the electronic excitation inside the molecule.

AFM manipulation of adsorbates on insulating surfaces
The Osnabrück group have used the RHK VT-AFM for a systematic study of the manipulation of water on CaF_2(111) at room temperature. With a simple line by line scanning at high detuning of -35Hz the deliberate translational manipulation of molecular water on the CaF_2(111) surface was achieved and the conditions where the defects were stationary while scanning (figure 1) were also identified.

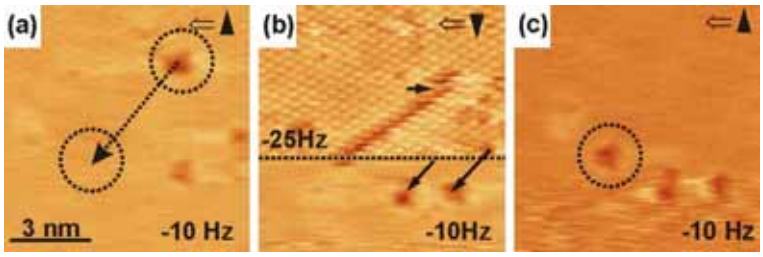

Figure 1 Controlled manipulation of a single water molecule towards two others.

One major result was that manipulation is along the main crystal directions on the surface, consistent with an adsorbate bound to specific surface sites and jumping from one equivalent site to the next neighbouring site. Careful examination of the manipulation path revealed a characteristic shape that was formerly observed in scanning tunnelling microscopy experiments. This so called "saw tooth" function has exactly the periodicity of the underlying calcium-lattice, further supporting our manipulation model. The first results of this work are now published in *Nanotechnology* **17** S148 (2006).

Manipulation of noble metal atoms and ions on thin film NaCl
A combination of low temperature and densty functional calculations has been used to study the properties of Au atoms and ions adsorbed on NaCl bilayers grown on a Cu(111) substrate (IBM Zurich and Chalmers). The charge state of single gold atoms may be controlled using a low temperature STM. The adsorption and diffusion properties of neutral and charged atoms are found to display striking differences showing that such properties may be controlled through the selectively charging atoms (Repp et.al. *Science* 305 493 (2004), *Phys. Rev. Lett.* **95** 225503 (2005)) – see Fig. 2..

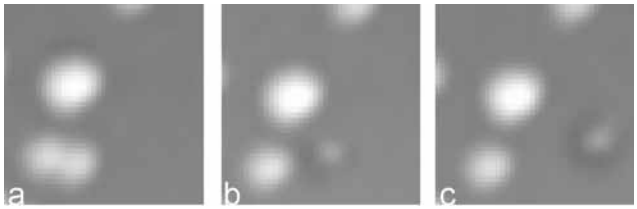

Fig 2. a: STM images of two single Au atoms and a Au dimer on NaCl. b: The Au atom on the right has been charged into a negative Au ion. (Au ion appears darker). c: The Au ion has moved to the right by thermal diffusion.

Vacuum deposition and manipulation of semiconductor nanocrystals

The Orsay group has demonstrated the deposition in vacuum of individual CdSe nanorods and explored their manipulation, i.e. translating or rotating, individual nanorods using the tip of the AFM either in the contact or tapping modes. On the hydrogenated C(100) surface, it has been found to be possible to dissociate or to rotate individual nanorods and these experiments show that the nanorods interact rather strongly with the hydrogenated diamond surface. For CdSe nanorods deposited on the graphite surface, (Orsay/Nottingham collaboration) imaging and manipulation requires relatively soft cantilevers (~ 1 N/m). Examples are shown below.

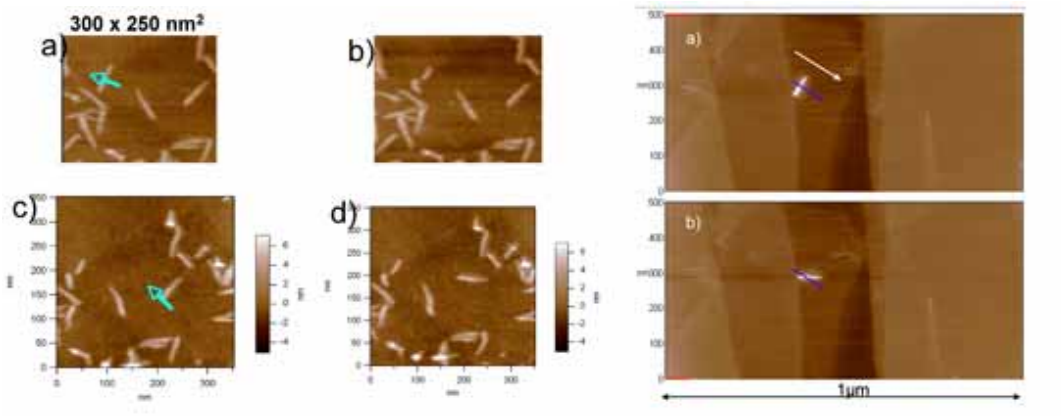

Figure3 : AFM manipulation of CdSe nanorods on a hydrogenated diamond C(100) surface. In figure a) and b) the arrow indicates the translation path of the AFM tip. The results of the AFM tip interaction with the nanorod are shown in b) and c) respectively.

Coupled bond breaking, rotation and translation in molecular rolling

We have identified the experimental signature of a rolling molecule in the manipulation of C_{60} on a Si(100) surface. The process couples bond breaking, rotation and translation and a simple model is verified using extensive density functional calculations. A modified process in which additional bonds are broken resulting molecular skewing will also be discussed. This work has been undertaken by the Nottingham and Kings groups (Keeling et.al., *Phys. Rev. Lett.* **94** 106014 (2005)).

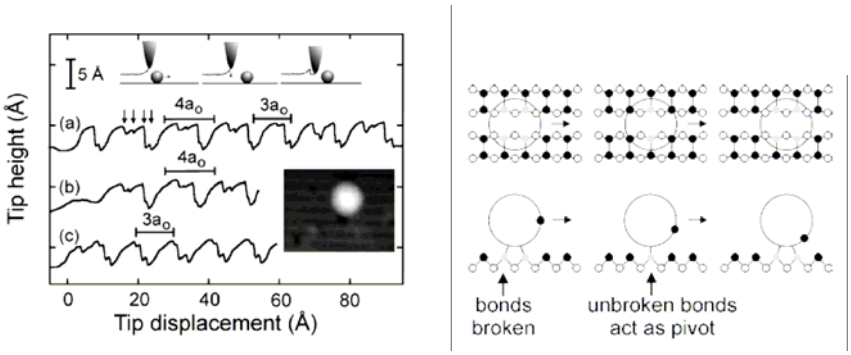

Figure 3 tip trajectories showing evidence for molecular rolling and schematic of the bond pivot process which couples rotation and translation on the Si(100) surface.

Numerical simulations of AFM imaging and tip-adsorbate interactions

Theoretical models for AFM probe-substrate and probe-adsorbate interactions which are relevant to both manipulation and imaging have been developed by the CNRS Toulouse, Kings and University College groups. These have been applied widely to AFM imaging of insulating surfaces such as MgO and CaF_2. Most recently a model based on atomistic modelling and kinetic Monte Carlo calculations has been developed to provide a generic basis for AFM induced manipulation of an oxygen vacancy on the MgO (001) surface (Trevethan et.al. submitted to *Phys. Rev. Lett.*).

*The consortium is co-ordinated by the University of Nottingham (P.H. Beton) and includes the following members: Bilkent University (lead scientist A. Oral), Chalmers University (M. Persson), CNRS Orsay (G. Dujardin), CNRS Toulouse (X. Bouju), IBM Zurich (G. Meyer), University College London (A. Shluger), Kings College London (L. Kantorovich), University of Osnabrück (M. Reichling).