Atomic manipulation of polyatomic molecules and size-selected gold nanoclusters

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Atomic manipulation - the extreme limit of nanotechnology - is most often performed at low temperatures on metal surfaces. Here by contrast I will discuss *variable temperature* atomic manipulation experiments on *semiconductor* surfaces, which reveal a variety of new phenomena (based on coupling of electron injection and thermal excitation). I will focus on a specific system – chemisorbed chlorobenzene (C_6H_5Cl or PhCl) on the Si(111)-7x7 surface – and discuss the bond-selective manipulation of the molecule via electron or hole injection. Specifically, I will report non-local atomic manipulation (leading to molecular desorption) of PhCl [2], which is effective over a length scale of 100Å or more and represents a kind of 'remote control' of atomic manipulation. This non-local electron attachment mechanism is also found to be thermally activated (barrier 0.4 eV), and suppressed by the proximity of the STM tip itself; both these results are explicable in terms of electron-driven excitation to an intermediate physisorbed state from which thermal desorption proceeds. Moreover C-Cl bond dissociation in the PhCl molecule is also thermally activated [3], with an energy barrier of 0.8 eV, which correlates with thermal excitation to the physisorbed (precursor) state of the molecule, where electron attachment occurs.

Our STM atomic manipulation experiments have also stimulated a new approach to the question of metastability in the atomic structure of size-selected nanoclusters, assembled from atoms in the gas phase and deposited in vacuum. These clusters might one day provide new routes to model catalysts, biochips, storage bits etc, but there are fundamental questions over their equilibrium atomic structures, since direct gas phase structural studies have been limited and new techniques like aberration-corrected scanning transmission electron microscopy (ac-STEM) are only now being applied to soft-landed, size-selected clusters. We will survey our latest ac-STEM experiments [6-11], which address the atomic structure of size-selected "magic number" gold clusters – Au_{20}, Au_{55}, Au_{309}, Au_{561}, and Au_{923}, with emphasis on dynamical manipulation experiments [9], which probe the transformation of metastable isomers into more stable configurations under the electron beam. The results establish a hierarchy of isomer stability as a function of size and provide a reference for theoretical treatments of nanosystems.

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