

## [총회초청 II]

### *MOLECULAR ORIENTATION, CRYSTALLOGRAPHY AND REACTIVITY IN CHEMISORBED SPECIES*

*N. V. Richardson, B. G. Frederick, F. M. Leibsle and S. Haq.  
Surface Science Research Center  
University of Liverpool  
Liverpool L69 3BX  
UK*

When molecules chemisorb on metal surfaces, a number of factors are involved in determining the molecular orientation, local bonding geometry and long range order. Relaxation and reconstruction in response to adsorption are already well described and more recently modification of step/terrace arrangements, involving significant mass transport across the surface have been shown to accompany chemisorption. Many of these studies have focussed on the behaviour of simple atomic adsorbates for which the establishment of long range order, permitting diffraction studies, is relatively straight forward.

Chemisorption of more complex, molecular species often/usually fails to produce long range order, this may be a consequence of the limitations of LEED (low energy electron diffraction) but large molecules, not surprisingly, require large unit cells; large at least relative to the substrate unit cell. This implies directly the possibility of many translational domains and a limitation in the size of individual domains unless diffusion of molecules occurs readily at the adsorption temperature or on subsequent annealing of the system. This, therefore, raises the question as to the relationship between molecular diffusion, molecular orientation at the surface and the degree of site specificity in the molecule/surface interaction. One also needs to question whether substrate atoms are sufficiently mobile to be a responsive part of the diffusion process.

Additional complexity in molecular chemisorption arises in multifunctional species. At the lowest coverages, each maximises its interaction with the substrate by an appropriate orientation and conformation; the molecule establishes a large "footprint" on the surface. However, large footprints imply low monolayer densities and, in the interests of further decreasing the enthalpy of the system it may be advantageous to increasing the density at the expense of the individual molecule/surface interaction and reduction of the footprint. The conformation/orientation of the adsorbed species will change, eventually allowing a single functionality to dominate the surface interaction. In the low coverage situation with a multifunctional molecule/surface bond, we anticipate relatively little site specificity, significant disruption to the substrate atomic arrangement and rather easy diffusion of the inhibit diffusion. These processes are important in determining the extent of long range order while the precise nature of that order and the structure of the unit cell is additionally influenced by interadsorbate interactions mediated by the surface.

In this presentation, these concepts will be developed using data obtained for the chemisorption of benzoic acid and related species on a Cu(110) single crystal surface, comprehensively studied by a combination of LEED, STM, EELS and FTIR.