2  Fundamentals of Adsorbate-Surface Interactions

Heinz Hövel, Lars S. O. Johansson, and Bruno Reihl

2.1  Introduction

Certain atomic and molecular species play the role of model systems for the understanding of fundamental chemical and physical concepts in adsorbatesurface interactions. Although the commercial value of these species may be rather low, their value must be appreciated by the conclusions which can be drawn from them, and their possible subsequent implementations into technical processes and/or the engineering of novel materials. Amongst these model species are the rare-gas atoms with their closed electronic shells, the alkali metal atoms with just one valence electron, the highly symmetric \( C_{60} \) molecule, and metal clusters, all adsorbed on the best-understood single-crystal surfaces. These are those of graphite, silicon, silver, and gold. Various combinations of these model systems and surfaces will be presented here with the special focus on the adsorbate-surface interaction, and the resulting modifications of both the adsorbed species and the substrate surface.

A key issue in this context is the question of bonding, its nature and strength. Weakly bound species may be desorbed from the substrate surface by a small energy transfer as, e.g., given by a small temperature increase. As an example, we mention xenon on graphite, which bonds by the Van-der-Waals interaction below 65 K. Usually, this is referred to as physisorption.

In the other extreme of a very strong bond, the energy equivalent of several hundred Kelvin is required to break the bond and allow the adsorbed species to desorb from the substrate surfaces. This bonding regime is usually termed chemisorption and comprises, e.g., alkalis and \( C_{60} \) on silicon, if we restrict ourselves to the above-mentioned list of model systems. The strong bonding case is usually accompanied by a charge transfer. Depending on the degree of localisation and direction of the involved electronic orbitals, the literature distinguishes ionic, covalent and metallic bonding [1].

For an understanding of the interplay between the electronic and geometric properties of the adsorbate–surface system it is important to know and understand the properties of the clean, possibly reconstructed surfaces, since the adsorbing species may induce or alter any reconstruction, which is then usually accompanied by a modification of the electronic structure, changing, e.g., the composite surface from metallic to semiconducting or vice versa. In most cases, the degree of surface modification is scaling with the bonding

strength: As we will discuss below, adsorbed xenon leaves the graphite surface unchanged, while C\textsubscript{60} adsorbed on the Au(110)\(1 \times 2\) surface causes a complete rearrangement of the top atomic layer, resulting in a new Au(110)\(1 \times 5\) reconstruction of the substrate underneath.

Besides the surface reconstruction, the adsorbate can form an ordered overlayer, which may or may not be in registry with the surface periodicity, and is usually dependent on the amount of adsorbed species and its interfacial morphology given by the overlayer–surface strain and annealing temperature applied. Important here is also the relative strength of the adsorbate–surface versus adsorbate–adsorbate interaction. For a strong bonding to the surface the overlayer forms a commensurate structure which fits into the surface periodicity. If the bonding within the adsorbed species is dominating, this leads to an incommensurate overlayer or even to three dimensional growth. As we shall show in the next section a submonolayer of xenon on graphite forms an incommensurate overlayer with a honeycomb-like domain structure.

### 2.2 Physisorption of Xenon on Graphite: Superstructure and Domain Boundaries

As an example for physisorption we discuss xenon on graphite. Monolayers of rare gases on graphite provide ideal testing grounds for 2D adsorbate phases and phase transitions [2], as they exhibit a large variety of different phases originating from the fact that the lateral interaction of the rare gas atoms is of the same order of magnitude as the corrugation of the graphite surface potential [3]. The phase diagram of Xe on graphite is well-known [4] along with many details in the monolayer-coverage regime [5]. Hong et al. [5] found a commensurate \((\sqrt{3} \times \sqrt{3})R30^\circ\) Xe phase for the monolayer coverage at temperatures below \(T = 60\) K, which was confirmed by other studies [4]. As the \((\sqrt{3} \times \sqrt{3})R30^\circ\) lattice constant is about 3\% smaller than the Xe bulk lattice constant, Xe forms an incommensurate phase in the submonolayer regime, because compressive strain would be needed for the formation of the commensurate phase.

The scanning tunnelling microscopy (STM) topograph in Fig. 2.1(a) shows an atomically resolved surface area of \(16 \times 16\) nm\(^2\) of xenon on graphite. It exhibits a nearest-neighbor distance of \(0.45 \pm 0.05\) nm in agreement with the expected \((\sqrt{3} \times \sqrt{3})R30^\circ\) value of 0.425 nm for a Xe adlayer on a graphite surface (for experimental details see [6,7]). The Xe atoms resolved in Fig. 2.1(a) form hexagonal patches about 15 atomic rows wide, separated by domain walls which appear in the STM signal as a smooth contrast several atomic rows in width. Xe atoms forming domain walls are slightly darker in the image than the surrounding Xe atoms in the domains. The origin of this contrast will be discussed below. The Xe domains are arranged in a hexagonal honeycomb-like structure. This is in agreement with an incommensurate phase observed for Xe coverages well below the completion of the first monolayer at tem-