Chemical reactions on surfaces can be followed in detail using X-ray photoelectron spectroscopy (XPS or ESCA), in particular in combination with scanning tunnelling microscopy (STM). From the XPS binding energies of the adsorbate and substrate core levels, detailed information on the chemical composition, chemical state (e.g. oxidation state), adsorption sites, but also on the photoemission process itself can be derived. STM provides information on surface order and intramolecular conformation but also on the chemical state. Based on the understanding obtained for simple adsorbate systems, now complex molecular systems can be studied in great detail. One specifically interesting group of materials are metalloporphyrins. These metallothetrapyrole complexes are versatile functional building blocks in many biological and biochemical processes. Moreover, there are several examples where such molecules were utilized in technical applications, retaining their highly functional nature within an inorganic framework. Examples include gas sensors, solar cells and catalysts. In this presentation the surface chemistry of porphyrins on metal substrates will be addressed. Specific topics are interplay between porphyrin-substrate and porphyrin-porphyrin interactions, the role of the substrate, surface diffusion, the synthesis of metalloporphyrin monolayers by direct metalation of free base porphyrins, and the attachment of axial ligands on the central metal ion of metalloporphyrins.


