The interaction of water with surfaces plays a major role in many processes in heterogeneous catalysis, the environment, atmosphere, and technology. Weathering of rocks, adhesion between surfaces, and ionic conductance along surfaces are among many phenomena that are governed by the adsorption of molecularly thin water layers under ambient humidities. The properties of these thin water films, in particular their thickness, structure, and hydrogen-bonding to the substrate as well as within the water film are up to now not very well understood. In addition, the properties of the bulk liquid/solid interface governs many processes in electrochemistry, corrosion, and the environment. In this talk we will discuss the application of ambient pressure X-ray photoelectron spectroscopy (APXPS) to study these phenomena, including the particular challenges of performing photoelectron spectroscopy experiments at realistic relative humidities, i.e. water vapor pressures in the Torr range. Examples of the application of APXPS that will be presented include the onset of hydroxylation and water adsorption on metals and metal oxides, the correlation of electrical potentials and surface chemistry in solid oxide fuel cells, and promising approaches to interrogate the liquid/solid interface, in particular the electric double layer, using photoelectron spectroscopy.