PHOTOELECTRON SPECTROSCOPY AND SURFACE CHEMISTRY

A. M. Bradshaw

Fritz-Haber-Institut der Max-Planck-Gesellschaft
1000 Berlin 33, Germany

D. Menzel

Institut f. Festkorperphysik der Technischen Universität
München, 8046 Garching, Germany

ABSTRACT

Photoelectron spectroscopy has fulfilled much of its early promise as a useful complementary technique in surface science investigations. In the present paper we review certain aspects of recent work, in particular, the application to adsorption phenomena on single crystal surfaces. It is found that excitation with monochromatic soft X-radiation produces core level spectra which can be used to give an overview of different chemisorption states. Because the binding energies corresponding to such spectral features are often characteristic of the chemical environment of the atom concerned, it is possible, for example, to differentiate between molecular and dissociative chemisorption of molecules such as carbon monoxide and formaldehyde adsorbed on metal surfaces. Certain relaxation effects specific to adsorbed layers can be identified. The use of the method in chemisorption and oxidation kinetics is also discussed. Valence level spectra generally excited by longer wavelength radiation give information on the molecular orbitals of the adsorbate complex. A precise identification of such orbitals and thus the construction of gas phase/adsorbed phase correlation diagrams is achieved by investigating the dependence of the spectrum on energy and state of polarisation of the incoming photons as well as on the photoelectric angular distribution. The much-investigated CO|Ni (100) system is discussed here as an example. The establishment of empirical orbital energy diagrams is considered a necessary prerequisite for further progress in chemisorption theory. Recent measurements of the adsorption of unsaturated hydrocarbons on transition metals demonstrate the sensitivity of UPS in fingerprinting chemical reactions on surfaces.
INTRODUCTION

The present paper concentrates on certain aspects of the application of photoelectron spectroscopy in surface studies. It is not intended to be a comprehensive review of that subject, but rather an attempt to indicate where such measurements have contributed and are continuing to contribute to our understanding of chemisorption. Most of the examples are taken from work performed under ultra-high vacuum conditions on clean metal single crystal surfaces: a deeper insight into adsorption processes on polycrystalline surfaces—a problem of paramount interest in surface chemistry and heterogeneous catalysis—must necessarily follow such investigations [1]. The conventional division of the subject into XPS (= X-ray photoelectron spectroscopy) and UPS (= ultraviolet photoelectron spectroscopy) will be avoided here, as it merely derives from the experimental choice of photon source. The increasing use of the continuum provided by synchrotron radiation makes the XPS/UPS distinction somewhat arbitrary. In this review we shall refer simply to core level and valence level spectroscopies; X-radiation is always sufficiently energetic to cause photoelectron emission from valence levels. Before considering examples of each experiment and the chemical information they supply, it is necessary to discuss in general terms the photoionisation process [2].

Let us picture electromagnetic radiation of sufficiently short wavelength incident upon a solid surface. The parameters characterising such radiation are its energy (inversely proportional to wavelength) and the orientation of its electric field vector \( \mathbf{E} \) relative to the co-ordinate system dictated by the surface. In the case of unpolarised radiation the relevant parameter is the angle of incidence, \( \alpha \). The emitted photoelectron is characterised by its momentum, \( \mathbf{p} \), or, alternatively, by its kinetic energy, \( E_K \), together with the polar and azimuthal angles, \( \theta \) and \( \phi \), locating \( \mathbf{p} \) in the surface coordinate system. For a single crystal surface of defined orientation the crystal azimuth must also be defined. This is particularly important for discussions of ordered adlayers. The photoelectron is energy-analysed under particular conditions of \( \theta \) and \( \phi \) and registered with a suitable detection system. For detailed information on experimentation the reader is advised to consult general reviews on photoelectron spectroscopy of surfaces [3-7] as well as the relevant texts on radiation sources [8,9], electron energy analysers [10] and ultra-high vacuum [11].

In general it is not possible to describe the photoionisation event in terms of a one-electron theory, even for atoms and molecules in the gas phase. Let us consider photoelectron emission from a particular orbital in a \( N \)-electron system. The relevant final state is the system of \( N-1 \) electrons and an electron with defined kinetic energy at infinity. The appropriate energy equation is thus