

## SYNCHROTRON RADIATION APPLIED TO SURFACE SCIENCE

D. MENZEL

*Physik Department E 20, Technische Universität München,  
D-8046 Garching, F.R.G.*

## Abstract:

A short survey of the main types of research made possible by synchrotron radiation in the field of surface science is presented and complemented by references to more detailed reviews. The combination of synchrotron radiation with high field methods is briefly discussed, and it is shown that the most promising topic should be the study of photo-field desorption.

Photon-induced processes have long been used for the investigation of surfaces, in particular of adsorbate layers. While the photon absorption process itself is not surface-sensitive because of the rather large mean free path of light in a solid ( $10$  to  $10^3$  nm depending on wavelength), secondary surface-sensitive probes can be used, the most important of which are emitted electrons (photoelectrons, Auger electrons, secondary electrons). Photon-induced excitations can, as in molecules, lead also to breaking of bonds, so that the detection of ions and neutrals set free by irradiation constitutes another surface-sensitive probe.

Photoelectron spectroscopies with line sources are among the most important methods for surface investigations /1/. Synchrotron radiation /2/ adds several advantages, the main ones being the continuously tunable frequency and natural polarization; the pulsed time structure can also be utilized. The upcoming generation of insertion devices (wigglers, undulators) /3/ will lead to improved energy resolution and the possibilities to measure spectra in very short times (making kinetic studies possible), and to focus the radiation into small spots (enabling one to develop surface scanning and imaging microscopes with all probes mentioned above).

The field of surface science with synchrotron radiation is very large, extending from very simple applications to very intricate ones. To start with examples of the former: in photoelectron spectroscopy of valence or core levels, the tunability of photon energy makes it easily possible to "tune" the surface sensitivity (for the same initial state, the photoelectron kinetic energy can be varied by variation of photon energy, and values with large or small mean free

paths in the solid can be selected, leading to emphasis on bulk or surface properties); to select ranges of advantageous cross section ratios (by tuning to photon energies for which the substrate valence levels have low photoionization cross sections because of a Cooper minimum /4/ or the like, the adsorbate states can be accentuated); or to simply distinguish electron emission from states of constant initial energy (binding energy) from those with constant final (kinetic) energy. By choice of the appropriate photon energy range, the derivation of two- and three-dimensional band dispersions from angle-resolved photoelectron spectroscopy can be greatly facilitated /5/. Resonances in photoionization cross sections for certain adsorbate levels can be measured and used, because of their definite symmetry, to derive the molecular orientation on the surface from polarization-dependent measurements, analysed with dipole selection rules. This can be done for valence levels with angle-resolved photoelectron spectroscopy, and the same principle is utilized in so-called NEXAFS (near-edge x-ray absorption fine structure) measurements for core excitations. To make the latter surface sensitive, Auger electrons from the decay of the wanted core levels are usually monitored. Applying a simple empirical rule, bond distances can even be estimated in this way /6/. The real realm of bond distance determination, however, is the SEXAFS (surface extended x-ray absorption fine structure) method /6,7/, which measures the modulation of photoionization cross sections as a function of photon (and therefore photoelectron) energy caused by constructive and destructive interference on the emitting center of the photoelectron wave backscattered from neighbouring atoms. Again Auger electrons can be used as a surface sensitive probe (the total secondary yield is less surface sensitive). Recently the fluorescence yield from surface atoms appears as a possibly superior probe /8/; and ions from subsequent bond-breaking have also been used /9/. The method is particularly powerful if full use is made of the polarization of light so as to "point" the emitted photoelectron towards a certain neighbouring atom. A similar type of interference in a somewhat different application is utilized in photoelectron diffraction /10/.

A new dimension of photoelectron spectroscopy is added if besides energy and direction, the spin state of the emitted electrons is analysed. With linearly polarized primary photons, magnetic properties of crystals and surfaces can be investigated /11/. If circularly polarized photons - obtainable from synchrotron light sources by going slightly out of the plane of orbiting electrons - are used, spinpolarized electrons can be obtained from non-magnetic materials. Using relativistic selection rules, spin-orbit split states and bands can be analysed this way /12/.

The combination of using synchrotron radiation of a certain energy and polarization to prepare a final excited state of well-defined energy and symmetry, with the detailed study of the decay products of this state is particularly promising for the understanding of the complicated many-body processes in surface layers. If the primary excited state is a core-excited state of an adsorbate, its electronic decay will liberate Auger electrons whose energy- and angle-dependent intensity can be used to assign the various two-hole states and study screening and shake-up in such layers /13/. We have concluded from such studies that in strongly coupled adsorbates the photoexcitation final state is not necessarily identical to the Auger initial state. In a next step, the two-hole or more complicated states produced by this Auger decay will often weaken the surface or internal bonds of ad-molecules sufficiently to liberate ions and neutrals /14/. The careful study of such desorption processes as functions of

photon energy and polarization, and their comparison to the spectroscopic information derived as described above have allowed to understand the mechanisms of such processes in quite some detail and to pinpoint the competition and possibly even interference of many-body processes (screening vs. Coulomb localization) /15/.

A totally different approach for surface structure studies is the recent development of surface x-ray diffraction, in particular using standing wave fields /16/.

If we ask ourselves which of these methods could be combined to advantage with high field techniques, it is obvious that the bulk of methods, working with the various types of electron spectroscopies, will not be usable, as photo-field emission promises new information only in the low energy region ( $h\nu < E_V - E_F$ ), while the domain of synchrotron radiation lies much higher. On the other hand, the combination of photon excitation with high ionization fields appears very interesting. In the simplest approximation (Born-Oppenheimer representation of states by potential curves; Franck-Condon transitions describing the photon absorption), a high field will as a first effect distort the potential curves, in particular those of the charged excited states. Furthermore, particles in these states will be strongly accelerated away from the surface. According to the accepted concept of electronically stimulated desorption, its probability is strongly influenced by "recapture" or "delocalization of the excitation" /15/ processes which depend dramatically on the time spent by the excited particle at a location close to the surface after excitation. Therefore, the decrease of dwelltime of the excited particle by a high field should dramatically enhance the desorption yield. In the case of physisorbed species, in particular rare gases, the desorption of ions should become possible (which cannot occur under zero field conditions, because a Van der Waals-bound atom becomes more strongly bound by ionization). On the other hand, the high field may directly influence the screening process mentioned above, as well as the neutralization, by pushing back the screening electrons into the substrate. It is not clear at present whether the Born-Oppenheimer representation is still valid under such conditions.

Photo-field desorption experiments with low light energies have already been carried out for some time /17/. Their extension to higher excitations appears of great interest. The experimental difficulties are quite high, as the synchrotron light beam has to be aimed exactly onto the tip proper, and more generally two tenuous techniques (high field, and synchrotron beam), each with their complexities and intrinsic stress, have to be made not only compatible, but also to work simultaneously. Nevertheless, first promising results have been obtained, as will be shown in the next paper, and more can be expected to come soon.

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