

Brundle C R. The application of electron spectroscopy to surface studies.

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The paper reviews the application of several types of electron spectroscopy to adsorption at surfaces. Areas considered are: how many atomic layers each type probes; what are the quantitative elemental analysis attributes; what degree of information is available on the electronic structure of the adsorbate/substrate complex; and what surface changes are induced by the measurements themselves. [The *SCI*[®] indicates that this paper has been cited over 145 times since 1974.]

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"In 1968 I was a postdoc at Bell Laboratories studying the electronic structure of small molecules by UV photoelectron spectroscopy (UPS). UPS determines molecular orbital structure directly by measuring the kinetic energies (KE) of electrons ejected from the molecular orbitals by monochromatic photon impact. The companion technique, x-ray photoemission (XPS), uses x-rays to photoeject electrons from more tightly bound atomic core-levels. The binding energies of these electrons are characteristic of the atom concerned, thus providing an atomic identification.

"I became interested in the interaction of molecules with surfaces through the stimulation of Homer Hagstrum who used my gaseous UPS spectra to help interpret his ion neutralization results for sulfur and ox-ygen atoms adsorbed on nickel.¹ It seemed to me that for solids UPS and XPS should be sensitive to *only* the first few atomic layers since ejected photoelectrons cannot travel far through a solid. XPS was, however, being commercially touted as a *bulk* analytical tool. On the other hand, Auger spectroscopy (AES), a closely related technique using

electron impact instead of x-rays, was established as a surface technique

"In 1970 I moved to a faculty position at Bradford University (England), to a department with surface chemistry and catalysis interests. I wrote an unpublished review before leaving Bell on the *potential* applications of electron spectroscopy to surfaces, which was used as the basis for a (successful) grant application in England. The review was then turned into a book chapter² and on the basis of this I was invited to the 20th National Symposium of the American Vacuum Society (1973) to give a review paper on UPS, XPS, and AES. The cited paper is the text of that address. Unlike the earlier review it contained much actual data since results were now forthcoming. One section of the review was a discussion of how many atomic layers the different electron spectroscopies (UPS, XPS, and AES) probed. This depends on the mean free path length for inelastic scattering, λ , of the ejected electrons. The smaller λ the thinner the surface layer from which these electrons can escape without suffering energy losses. I tabulated literature λ 's (from XPS, UPS, and AES work) and plotted them against electron KE. The main intent of the plot was to demonstrate that the experimental λ 's were a strong function of KE, but *independent* of whether the spectroscopy was XPS or AES. For a given KE, XPS is just as surface sensitive as AES.

"Seventy percent of the citations concern the A versus KE plot, usually to establish the surface sensitivity of the measurements being performed. More extensive collections of data are now available. The most recent and comprehensive is by M.P. Seah and W.A. Dench.³ It is interesting to note that the original commercial XPS instrument, designed for *bulk* analysis, disappeared from the market after a few years, being quite unsuited for the surface work to which the technique should be applied, whereas a plethora of companies now market expensive ultra-high vacuum instruments for the rapidly expanding and well-funded surface science field "

1. Hagstrum H D & Becker G E. Orbital energy spectra of electrons in chemisorption bonds—O, S, Se on Ni (100). *J. Chem. Phys.* **54:**1015-32, 1971.

2. Brundle C R. The application of electron spectroscopy to surface studies. *Surface and defect properties of solids.* (Roberts M W & Thomas J M, eds.) Washington, DC: American Chemical Society, 1972. Vol. 1, p. 171-204.

3. Seah M P & Dench W A. Quantitative electron spectroscopy of surfaces: a standard data base for electron inelastic mean free paths in solids. *Surface Interface Analysis* **1:2-11**, 1979.