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Commentary on photoelectron, Auger electron, and metastable de-excitation spectroscopy

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I believe that we should look in particular at the many newly available directions that the first three speakers have indicated.

Professor Siegbahn's paper sets out the state of the art in photoelectron spectroscopy. It constitutes an experimental *tour de force* and will serve as an inspiration to all experimentalists. The study of liquids is a particularly fascinating area that he has touched on, although it falls outside the scope of this discussion.

Photoelectron spectroscopy (photoemission in the terminology of the physicist) has an unrivalled ability to describe the bonding of an adsorbate to a surface. Carbon monoxide on nickel, to which Professor Siegbahn referred briefly, represents a classic example, but not, alas, an archetype (Allyn *et al.* 1977; Davenport 1976; Eastman & Cashion 1971). During the 1970s the full details of the bonding and of the bonding site and geometry were unravelled by photoelectron spectroscopy, almost without reference to any other technique. To achieve this high level of understanding required a prodigous amount of experimental and theoretical work. It is disappointing that the same level of effort has not been applied to many other adsorption systems of equal general interest.

Professor Siegbahn's studies open up the possibility of examining surfaces and interfaces at very high resolution. His brief description of the Pt/Si interactions, where he suggests that the Schottky barrier is situated one monolayer below the Pt/Si junction, is particularly fascinating. So also is the possibility of performing time-resolved studies by using light from synchrotron sources. One can envisage a whole range of experiments where the sample is excited by a laser pulse and studied by photoelectron spectroscopy or, of course, vice versa.

Professor Rao's paper (kindly read by Professor Thomas in Professor Rao's absence) exemplifies the well established chemical tradition of extracting valuable knowledge from semi-empirical relations. Professor Rao explores three approaches to the very difficult problem of deducing chemical information from Auger electron spectroscopy. The first and simplest uses the ratio of intensity of two Auger peaks, one of the type ($C_1\,C_2\,V$) and the other (C_1, C_2, C_3), where C refers to a core level and V to a valence level. Professor Rao has summarized the studies of his group over a number of years and shown that the number of metal valence electrons, which I take to be a shorthand for oxidation state, can readily be determined. These studies provide the promise of extraction of chemical information from small areas such as can readily be studied in the scanning transmission electron microscope (s.t.e.m.). The approach using Auger peak intensity ratios is particularly promising, since it should not require high-resolution spectra. By contrast, Professor Rao's studies of what he calls inter-atomic Auger transitions represent an experimentally difficult challenge, although essentially aimed at the same target.

The studies of shape changes in Auger spectra are also of great interest. It seems that these

Auger spectra should represent the self-convolution of the valence band density of states of the adsorbed species. In this they are similar to Professor Ertl's metastable de-excitation spectra, obtained when the resonance neutralization and Auger decay mechanism is operating. The Auger fingerprint should have the advantage that contributions from the substrate will be small. I wonder if any group has the courage to attempt this deconvolution, for which Hagstrum & Becker (1971) have provided a recipe, and which Professor Ertl has shown can be usefully applied.

Professor Ertl's contribution reminds us that the first electron spectroscopic technique to give clear information on the valence band density of states of metals and absorbates was ion neutralization spectroscopy, developed by Hagstrum (1972). Professor Ertl uses molecular beam technology to generate excited inert gas atoms. These have lower kinetic energies than the ions used in ion neutralization spectroscopy, so that the technique of metastable de-excitation spectroscopy (also known as surface Penning ionization electron spectroscopy, or s.P.i.e.s.), has greater surface sensitivity.

Professor Ertl has provided evidence that the metastable atom may undergo de-excitation by two mechanisms. Where resonance ionization is followed by Auger neutralization, the resulting spectrum approximates to the self-convolution of the density of states. Professor Ertl has shown that this can be unfolded to deduce information on surface states lying near the Fermi level. Probably of greater interest is the case where the excited electron in the inert gas atom is prevented from tunnelling into the solid, for example by an adsorbed layer. The de-excitation process of Penning ionization then involves only one electronic level from the solid and the resulting electron spectrum relates directly to the density of states. Professor Ertl assumes that complete switch-over occurs from one de-excitation mechanism to the other. It is tempting to wonder if this is always the case, particularly when the adlayer coverage is small. It is also difficult to predict when an adlayer will prevent resonance neutralization. In Professor Ertl's study of acetylene on Pd(111) this change in mechanism does not occur for α and β adsorbed states of acetylene, but only happens when the transformation into adsorded benzene fragments takes place (Sesselmann *et al.* 1983).

Professor Ertl shows convincingly that the contribution to the spectrum from the metal band structure, so often dominant in ultraviolet photoelectron spectroscopy, can be removed in the metastable de-excitation spectrum. This represents a major strength of the technique. Of great interest is his observation of a peak close to the Fermi level in adsorbed caesium. He attributes this to occupancy of the Cs 6s level, and therefore proof that the caesium is not fully ionized. This conclusion is in accord with work function studies of adsorbed alkalis at high coverage.

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