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APPLICATIONS OF AUGER AND PHOTOELECTRON SPECTROSCOPY

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APPLICATIONS OF AUGER AND PHOTOELECTRON SPECTROSCOPY

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APPLICATIONS OF AUGER AND PHOTOELECTRON SPECTROSCOPY

I. Introduction

This is a very simple-minded presentation which is the only way I know how to make a presentation.

II. Principles

First, let me briefly refresh your memory on the principles involved in Auger and Photoelectron Spectroscopy. As you know, if we excite an atom by ejecting one of its inner-shell electrons, the vacancy will be filled by an electron from one of the outer shells. This process is shown schematically in Figure 1. The energy released in this transition is either emitted as a photon – the characteristic or fluorescence x-ray, or transferred to another outer shell electron and in turn ejecting it. This second ejected electron is the so-called Auger

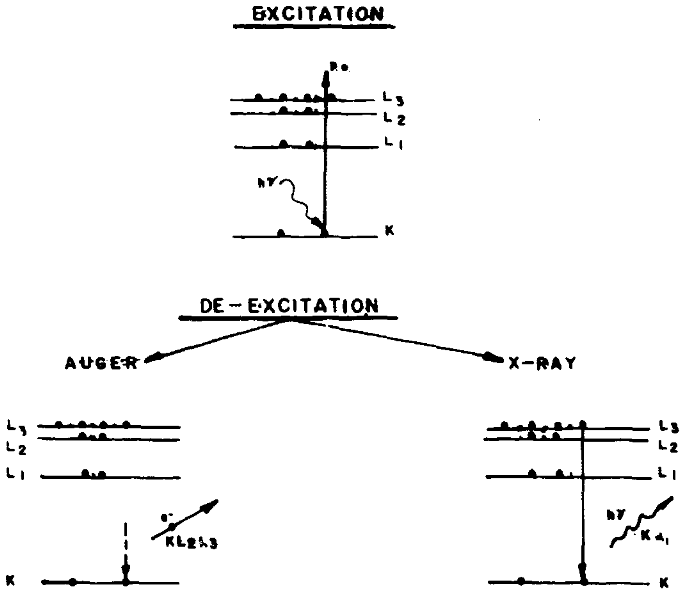

Figure 1–Schematic showing the principles involved in the excitation and de-excitation of an atom which give rise to the emission of characteristic x-rays as well as Auger electrons and photoelectrons. hv designates monoenergetic x-rays; p.e. designates photoelectron.

electron. Like the characteristic x-rays, Auger electrons are also monoenergetic and characteristic of the atomic species. In this respect Auger spectroscopy is quite analogous to x-ray emission spectroscopy. It so happens that for light elements Auger electron emission is the predominant mode of de-excitation rather than x-ray emission. In Mg, for example, the K fluoresence yield is only 1.3% which means that when a vacancy in the K shell of Mg is being filled, on the average 99% of the time Auger electron is emitted; only 1% of the time a fluorescence x-ray is emitted.

The energy of the characteristic x-ray is just the different in the binding energy of the two shells involved in the transition. For example, $E_{K\alpha_1} = E_K - E_{L_{III}}$, where $E_{K\alpha_I}$ is the energy of the $K\alpha_I$ x-ray and E_K and $E_{L_{III}}$ are the binding energies of the K and L_{III} shells respectively. Because of certain selection rules there are only two characteristic x-ray lines associated with the L to K transition of an atom, ignoring satellites. For the Auger electrons, the situation is a little more complicated. Even with K and L shells, the number of Auger lines varies from 5 for the light elements ($Z < 20$), to 9 for the intermediate elements ($Z \sim 40$), to 6 for the heavy elements ($Z > 90$). Figure 2 shows the first full 9-line KLL Auger spectrum observed by Hörnfeldt[1] and his colleagues in 1962 for Zr ($Z = 40$). One would expect the energies of the Auger lines are also more difficult to compute. However, a good approximation of the strongest Auger line KL_2L_3 can be obtained by the formula $E_{KL_2L_3} = E_K - E_{L_{II}} - E'_{L_{III}}$ where $E'_{L_{III}}$ is the L_{III} shell binding energy of the next higher element.

So far we have concentrated only on the deexcitation of an atom. What are some of the ways to create the initial vacancy to excite an atom? The easiest way is to make use of radioactive sources where a K electron is either swallowed by the nucleus – K-capture – or is kicked out of the atom in the process of nuclear deexcitation-internal conversion. Fe^{55} for instance is a K-capture source which leaves a hole in the K shell of its daughter Mn^{55} and both Mn K x-rays and KLL Auger electrons are emitted. However, there are only a few of such convenient radioactive sources.

A more popular way of excitation is by means of x-ray or electron bombardment. This way, as long as the x-ray or electron has sufficient energy, all elements and all shells can be excited. Furthermore if one uses monoenergetic x-rays for excitation one gets a bonus in the electron spectrum. This is because the electron which is ejected from the atom by the x-ray – the photoelectron – will have a kinetic energy exactly equal to the difference between the x-ray and the binding energy of the atomic shell from which it is ejected as shown in Figure 1. Therefore the photoelectron spectrum also contains information about the atomic shells and the atomic species. There are however two important differences between the photoelectron spectrum and the Auger spectrum. First,

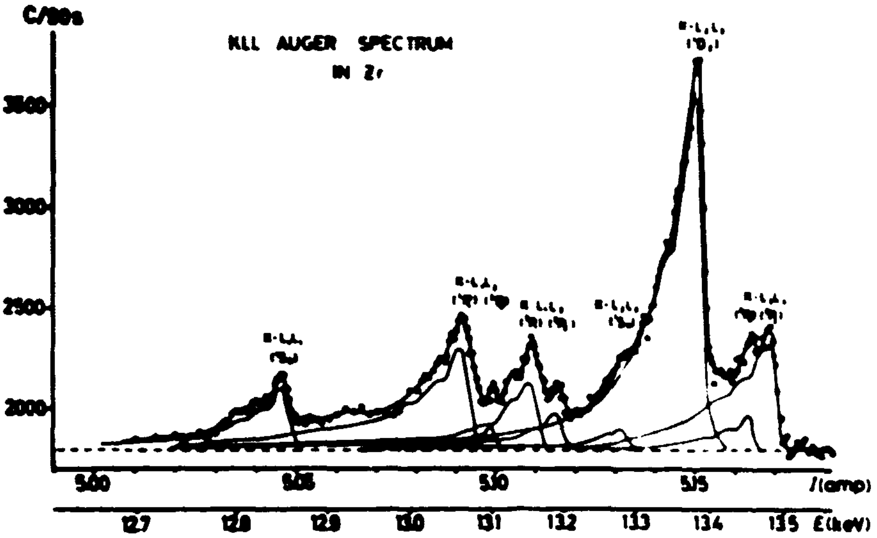

Figure 2–The first full 9-line KLL Auger spectrum observed by Hörnfeldt and his colleagues in 1962 for Zr (Z = 40).

for a given x-ray energy we get only one photoelectron line from each shell; whereas vacancy in one shell results in a series of Auger lines as mentioned earlier. Secondly the photoelectron energy is directly proportional to the energy of the x-ray that ejects it so that one can vary the photoelectron energy by using different energy x-rays. On the other hand, the energies of the Auger lines are independent of the incoming x-ray energy.

Of course excitation is also possible with other particles such as protons, α particles, etc. The difficulty lies in the production and intensity of these particles; but there are also advantages. In fact we are currently investigating the possibility of α-excitation.

Perhaps I have been a little misleading about the monoenergetic Auger and photoelectrons. It is true that they are monoenergetic when they are ejected from the atom, but in a solid material the vast majority of them will have undergone many energy-loss collisions before they can emerge and be analyzed. Because of this, the actual spectrum of monoenergetic electrons from a solid sample will have a continuum on the low energy side as shown in Figure 3. This is the spectrum we obtained from graphite sample bombarded by Al Kα x-rays. Both the carbon Auger and photoelectron peaks are visible; and note the shapes of the peaks. However, in trying to emerge from a solid the electrons actually lose their energies in discrete increments through various processes such as the excitation of atoms, molecules, valence electrons or collective plasma oscillations

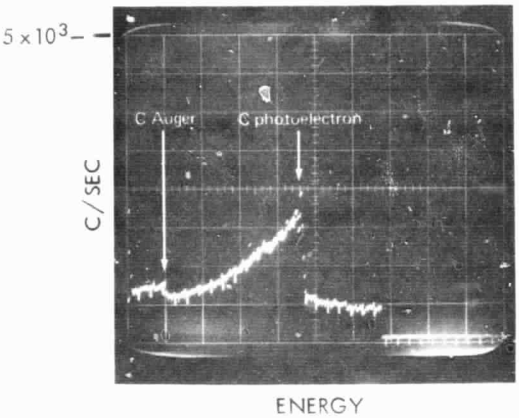

Figure 3—Auger and photoelectron spectrum of graphite sample using Al Kα excitation, coarse resolution. Note the continuum on the low energy side of the peaks.

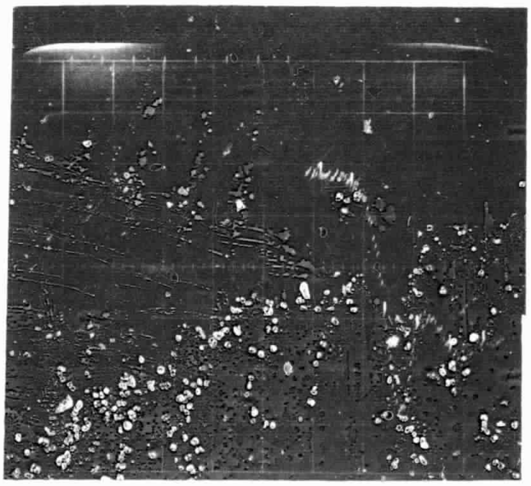

Figure 4—The photoelectron line of Figure 3 under high resolution. Note the valley on the low energy side of the peak as a result of discrete energy loss.

Because of this, if the spectrometer has high enough resolution the continuum on the low energy side does not go all the way to the peak but dips down to a minimum just before it reaches the peak. Figure 4 shows the carbon photoelectron peak of the same graphite sample at much higher resolution. It was the fortunate presence of this discrete energy loss valley which allowed people to determine accurately from the undistorted peaks the precise energies of the electrons.

III. Instrumentation

How are the Auger electrons and photoelectrons analyzed? There are mainly two types of electron spectrometers; one is magnetic, the other electrostatic.

Magnetic:

$$mv = eB\rho$$

$$\frac{\Delta(mv)}{mv} = \text{constant}$$

Electrostatic:

Cylindrical: $$eV = 2E \ln\left(\frac{R_o}{R_i}\right)$$

Spherical: $$eV = E\left(\frac{R_o}{R_i} - \frac{R_i}{R_o}\right)$$

$$\frac{\Delta E}{E} = \text{constant}$$

Let $$x \equiv \frac{R_o - R_i}{R_i} \ll 1, \quad \text{then}$$

Cylindrical: $$eV = 2Ex - Ex^2 + \cdots$$

Spherical: $$eV = 2Ex - Ex^2 + \cdots$$

Figure 5–Basic equations governing magnetic and electrostatic electron analyzers.

e, m, v, E: charge, mass, velocity, energy of electron.

B: applied magnetic field.

ρ: circular radius of electron path in a homogeneous magnetic field.

Ro, Ri: Outer, inner radii of metal plates.

V: applied voltage between plates.

In the simplest form the equation which governs magnetic spectrometers is shown in Figure 5. This is for an electron with charge e in a homogeneous magnetic field B, and circular orbit of radius ρ. As you can see, the momentum mv of the electron is proportional to the applied magnetic field B so that they are really momentum analyses. Another thing to note is that the percentage momentum resolution $\Delta(mv)/mv$ for each instrument is a constant. By carefully making the magnetic field non-homogeneous in a special way, the magnetic spectrometers can be made to have focussing properties in two planes – "double-focussing." It was through the improvement and design of these double-focussing β-spectrometers for nuclear physics, that gave birth to the present day high resolution, high transmission, low energy Auger and photoelectron spectroscopy about 12 years ago. The momentum resolution achievable nowadays is 1 part in 10^{-4} or 0.01%. Energy resolution is twice that. Instruments of this type are usually very large, with enormous Helmholtz coils surrounding them to cancel the earth's magnetic field and located in rooms completely free of iron. That is why there are only a few such instruments in the world.

In general the electrostatic spectrometers are either made from two concentric spherical metal plates or two concentric cylindrical metal plates. When a specific voltage is applied between the plates only electrons with a particular energy can fly through the gaps without hitting either plate. The basic equations governing these two types of electrostatic analyzers are shown also in Figure 5. Ro and Ri are respectively the radii of the outer and inner plates. We see that in either case the energy E of the electron is proportional to the applied voltage V so that these are truly energy analyzers. Also note that the percentage energy resolution of an instrument, $\Delta E/E$ is a constant. These equations look very different. However if the separation of the plates is very small compared to the radius of the inner plate

$$\frac{R_0 - R_i}{R_i} = x \ll 1$$

after a little arithmetic we find that the two types are really pretty much the same up to second order in x. For high resolution instruments this condition is usually satisfied so that the major difference between the two is that the clyndrical type focusses at 127° ($\pi/\sqrt{2}$) and the spherical type focuses at 180°. From spherical symmetry it is easy to see that the spherical analyzers is naturally double-focussing.

In principle the electrostatic analyzers can be made to have comparable performance as the magnetic analyzers, except these are much smaller and easier to build. Why weren't they popular then? First of all, at high voltages they may arc over so that one can't use them to analyze high energy electrons of say around 100 Kev or more. Secondly at high energies the relativistic mass increase of the electrons tend to destroy the focussing properties. So, although the principle of electrostatic analyzers have been known for many years they never become popular in nuclear physics which was the field they were intended for originally. Of course at photoelectron and Auger electron energies – from a few keV down, all these problems disappear. Now electrostatic analyzers have achieved energy resolution as good as 0.05%. Spectrometers with few 1/10% to 1% resolutions are common.

A third type of electrostatic analyzers make use of retarding potentials. A retarding grid by itself really measures the intensity distribution of electrons with energies above the retarding voltages. In order to derive energy distribution one has to plot the slope of the data vs. retarding voltage, i.e. differentiate the data. In this sense retarding potential analyzer is an indirect energy analyzer. However in 1964 Spicer and Berglund [2] came up with a scheme to accomplish the differentiation electronically while the retarding potential is being varied so that the data gave directly the energy distribution of the electrons. This is done by superimposing a small AC voltage on top of the dc retarding voltage ramp and record only the AC component of the electron intensity. Thus only the incremental change in the electron intensity as a result of an incremental change in the retarding voltage about a certain value is measured. This is really a long way of saying differentiation. This type of analyzer has of course very large solid angle because practically half of the sample can be seen. There is a more practical reason for such an analyzer, that is, such an analyzer has already been in existence in low energy electron diffraction (LEED) work. In LEED, the retarding grid is used to bias out the inelastically scattered electrons and the elastic ones are accelerated to a phosphor screen to produce visible light patterns. So it is not too much trouble to modify such a system to look at the energy distribution of the electrons. This system has the advantage of looking at the LEED pattern and the Auger spectra under identical environmental conditions. This type of modified LEED system is already quite popular.

The availability of electrostatic spectrometers, because of their small size and relative ease of manufacture brought Auger and photoelectron spectroscopy within the reach of everyday laboratories. The large number of potential applications has generated an enormous amount of interest in this field in the last couple of years.

IV. Applications

I'll try to outline a few of the applications of Auger and photoelectron spectroscopy.

As I mentioned earlier if monoenergetic x-rays are used for excitation one can determine very accurately the binding energies from the photoelectron spectra. Prof. Siegbahn's group in Sweden has measured some 300 levels of elements all over the periodic table. For light elements this new precision method found that old L_I shell values were off sometimes by as much as 50%. The instrumental resolution was so good that some workers had actually measured the atomic level width from the width of the photoelectron line and deduce the level life time using the uncertainty principle. Of course once the binding energies are accurately known one can turn around and depend on them in Auger and photoelectron spectroscopy for the identification of elements and levels, the determination of chemical shifts not to mention other related fields such as x-ray spectroscopy and internal conversion β spectroscopy.

Naturally a lot of work has been done on the Auger transition itself. Because the high resolution instruments made it possible to look at the details of the Auger transition, such as the 9-line spectrum we saw before, theorists and experimentalists have both been busy in trying to understand the basic physics of Auger transitions. As of now, this is by no means a closed subject, people like Asaad, Mehlhorn, Albridge, Krause (to name a few) are still deeply involved in this basic research.

In a chemical compound, the outermost or valence electrons of atoms participate with neighbors to form chemical bonds – ionic, partially ionic or covalent. This bonding influences the distribution of charges in the outer shell which in turn affects the screening of inner electrons. The result is a change or shift in the inner shell binding energies. This shift has been seen in x-ray emission spectroscopy. However, since the energy of the emitted x-ray is the difference between two levels, if both level suffer a binding energy shift of comparable magnitude (such as K and L shells) the net difference is rather small. Furthermore in light elements such as carbon, the emission line is broad to begin with due to the band width of the outer levels, any shift due to chemical bonding is difficult to observe. This is good advertisement to do photoelectron spectroscopy because a photoelectron is associated with a single sharp inner level, not the difference of two levels, so that the chemical shift is much more pronounced. Elements such as C, O, N, S which are important in organic chemistry are especially interesting candidates. Figure 6 shows the photoelectron spectrum of ethyl trifluoroacetate excited with Al Kα x-ray by Siegbahn's group.[3] The 4 carbon atoms in 4 different valence states show up as 4 different peaks. Conversely, the position of the chemical shift can be used to estimate the effective atomic charge in a molecule or solid and from that estimate the character of the chemical bond. I must also mention that although x-ray emission is not very sensitive to chemical shifts, because it involves the difference of two levels. Auger emission is sensitive because it involves 3 levels: one shell is involved twice, e.g. the L sheel is KLL transition. This has been observed.

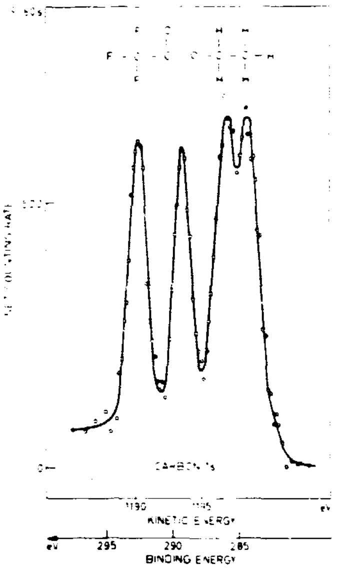

Figure 6–The photoelectron spectrum of the four valence states of carbon in ethyl tri-fluoroacetate using Al Kα excitation as observed by Siegbahn's group.

While we are talking about molecules, photoelectron spectroscopy is also being used to study the vibrational levels of molecule ions. These are extremely low energy levels of just a few eV with separations of .1 or .2 eV. In this case UV radiation, say the 584 Å (22 eV) He line, is used to excite a gaseous sample. Figure 7 shows a portion of the vibrational levels of O_2 molecule as observed by Turner[4] in England. This is obtained with a cylindrical electrostatic analyzer. Seigbahn's group, using electrostatic spherical analyzer, claimed to have seen even rotational fine structure on the side of vibrational levels! It is interesting to note that at these low energies, since $\Delta E/E$ = constant, ΔE is extremely narrow. The ΔE resolution of Figure 7 is about 0.01 eV.

Since photoelectrons can be ejected from any level as long as the photon has sufficient energy, band electrons below the Fermi level can also be excited. Their binding energy being only a few eV, their kinetic energy is just below the high energy limit of a photoelectron spectrum. Knowing the photoelectric cross section one should be able to derive the density of state information from the intensity distribution of these band electrons. Some preliminary work has been reported by Siegbahn's group using x-ray excitation, but more promising still is the use UV excitation because of the low photoelectron energy which means that ΔE would be much narrower as mentioned before. I heard that Spicer at Stanford is doing some work in this area using UV excitation.

We know that the range of low energy electrons in a solid is very small. Most of the Auger and photoelectrons which come out of a solid sample originate from very near the surface of the sample. Out of these, those few which come

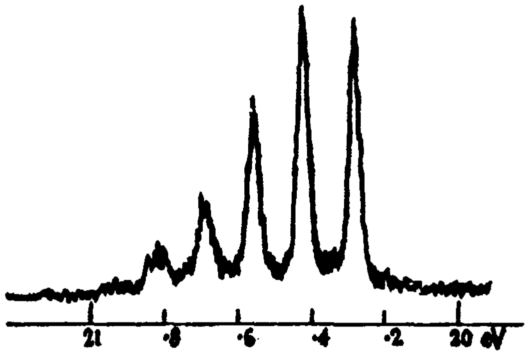

Figure 7–A portion of the photoelectron spectrum of O_2 excited with 584Å line of He showing vibrational levels as obtained by Turner.

out without energy loss, and on which we depend for identification, must originate near the top few 10's of Å. Naturally Auger and photoelectron spectroscopy should be a very sensitive method in surface studies. In the last year or two there has been a tremendous interest in this field using electron excitation. The advantage of electron excitation is that the existing electrons also have very little range, much smaller than x-rays at comparable energies, so that only the very top surface can be excited. The other advantage is, as I mentioned before, that it is already available in the existing LEED systems. When using electron excitation, the scattered primary electrons form a huge continuous background so that the discrete Auger peaks appear as tiny wiggles. In order to bring these peaks out of the slowly varying continuum Harris[5] at G.E. used the electronic differentiation technique we discussed earlier. Figure 8 shows a spectrum by him with, and without differentiation. Applying this technique to a LEED system, which is where most surface studies are being done, means double differentiation — once to get the energy distribution twice to bring out the peak positions. This is essentially what most people in the surface and LEED field are doing. At the physical electronics conference last week at Yale, various people showed that the Auger spectrum is sensitive to about 1% of a monolayer on the surface of crystals and that its intensity is essentially linear with coverage. Other people also reported that they have detected surface contaminants with the Auger spectrum without observing any change in the LEED pattern. It is obvious then that Auger spectroscopy can be used to monitor surface contaminants, impurity concentrations in semiconductors, surface diffusion, adsorption and desorption processes and many other related surface phenomena.

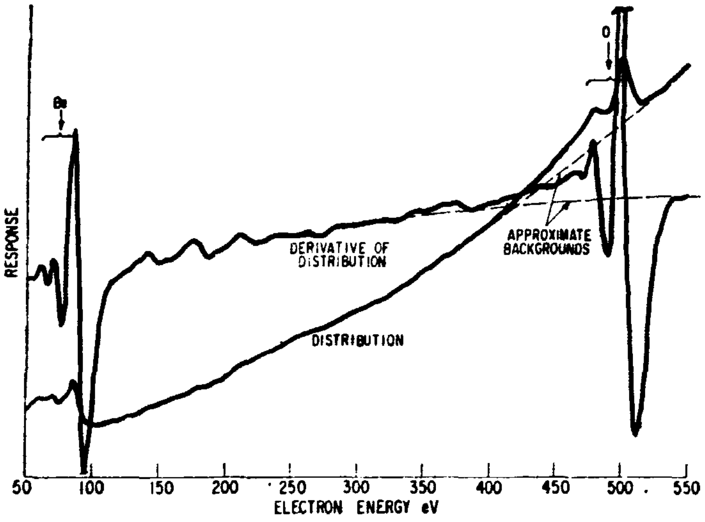

Figure 8–Auger spectra obtained by Harris using electron excitation with, and without electronic differentiation.

I hope I have given a few highlights in the Auger and photoelectron spectroscopy field. Judging from the amount of literature appearing on the subject and the papers presented at last week's conference this is indeed a very promising and exciting field of spectroscopy.

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