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Electron Spectroscopy for Atoms, Molecules, and Condensed Matter

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In my thesis (*1*), which was presented in 1944, I described some work I had done to study β decay and internal conversion in radioactive decay by means of two different principles. One of these was based on the semicircular focusing of electrons in a homogeneous magnetic field, the other on a big magnetic lens. The first principle could give good resolution but low intensity, and the other just the reverse. I was then looking for a way to combine the two good properties into one instrument. The idea was to shape the previously homogeneous magnetic field in such a way that focusing would occur in two directions, instead of only one as in the semicircular case.

It was known that in betatrons the electrons performed oscillatory motions in both the radial and axial directions. By putting the angles of period equal for the two oscillations, Svartholm and I (*2, 3*) found a simple condition for the magnetic field form required to give a real electron optical image; that is, we established the two-directional or double focusing principle. It turned out that the field should decrease radially as $1/\sqrt{R}$ and that double focusing should occur after $\pi\sqrt{2} \sim 255°$. A simple mushroom magnet was designed, the circular pole tips of which were machined and measured to fit the focusing condition. ThB was deposited on a wire net and put into position in the pole gap. A photographic plate was located at the appropriate angle and the magnet current set to focus the strong *F* line of ThB on the plate. The first experiment gave a most satisfactory result. Both the horizontal and the vertical meshes of the wire net were sharply imaged on the plate.

A more detailed theory for the new focusing principle was worked out and a large instrument with radius $R = 50$ centimeters was planned and constructed (*4*). Due to the radially decreasing field form an additional factor of 2 was gained in the dispersion, compared to the homogeneous field form. Since all electrons, for reasonably small solid angles, were returning to the symmetry plane of the field at the point of focus, no loss in intensity was experienced by increasing the radius of curvature of the instrument. Very large dispersion instruments with good intensity and much improved resolving power could therefore be designed to record β spectra and internal conversion spectra from radioactive sources. The magnetic double focusing was convenient for the fairly high-energy electrons (50 kiloelectron volts to 2 megaelectron volts) normally occurring in radioactive decay and the field form could easily be achieved by means of shaping the poles of an iron magnet. In my laboratory and in many other nuclear physics laboratories, double focusing spectrometers frequently became used for high-resolution work (*5*). This type of focusing was also used subsequently by Hofstadter (*6*) in his well-known work on high-energy electron scattering from nuclei and nucleons.

From the late 1940's through the early 1960's I was much involved in nuclear spectroscopy. This was a particularly interesting and rewarding time in nuclear physics since the nuclear shell model, complemented with the collective properties, was then developed, to a large extent founded on experimental material from nuclear decay studies. Nuclear disintegration schemes were thoroughly investigated, and the spins and parities of the various levels were determined, as well as the intensities and multipole characters of the transitions. During this period the discovery of nonconservation of parity added to the general interest of the field. Also, the form of the interaction in β decay, which appeared originally in Fermi's theory, was extensively investigated. A large part of my own and my students' research was therefore concerned with nuclear spectroscopy of radioactive decay (*7–23*). In 1955 I edited a volume (*24*) on *Beta- and Gamma-Ray Spectroscopy*. In 1965 I concluded my career as a nuclear spectroscopist by publishing (*25*) *Alpha-, Beta- and Gamma-Ray Spectroscopy*. In this extensive survey of nuclear spectroscopy I had been able to collect the prodigious number of 72 coauthors, all prominent authorities and in many cases pioneers in the various fields. Although my own scientific activity at that time had become almost entirely directed toward the new field which is the subject of this article, I have kept my interest in nuclear physics alive as the editor of the journal *Nuclear Instruments and Methods in Physics Research* since its start in 1957.

Photoelectron Spectra

Let me now return to the situation around 1950. At that time my co-workers and I had for some time been exploring the high-resolution field by means of our large dispersion double focusing instrument and other methods, such as the high transmission magnetic lens spectrometer and coincidence techniques. Often, however, my experimental work had to stop and wait for radioactive samples, the reason being a capricious cyclotron. It then came to my mind that I

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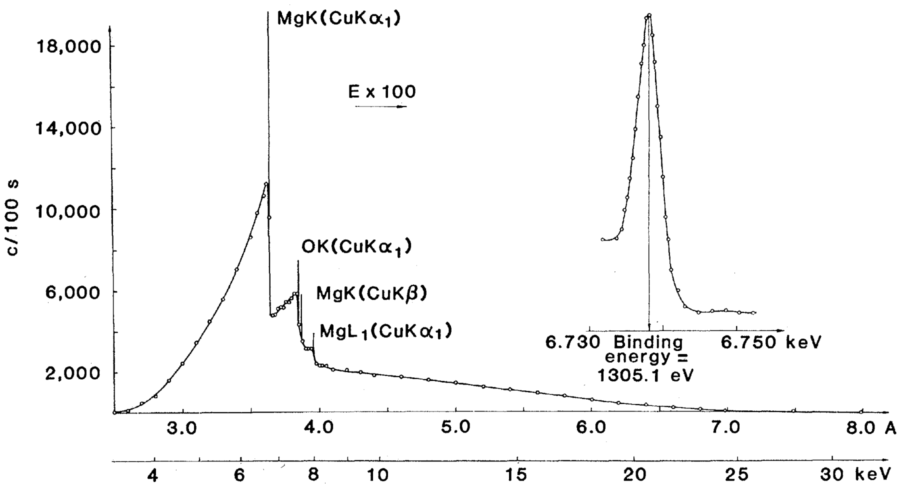


Fig. 1. Electron spectrum obtained from MgO with Cu x-radiation. Edges are found at energies corresponding to atomic levels of magnesium and oxygen. A very sharp electron line can be resolved from each edge. Such an electron line is shown in the inset with the energy scale expanded by a factor of 100 to bring out the finite width of the line.

should try to simulate the radioactive radiation by a substitute which I could master better than the cyclotron. I had found that a convenient way to accurately investigate gamma radiation from radioactive sources was to cover them with a γ-ray–electron converter, a thin lead foil which produced photoelectrons to be recorded in the spectrometer. I now thought that I should instead use an x-ray tube to expel photoelectrons from ordinary materials, in order to measure their binding energies to the highest possible accuracy.

In my nuclear physics work such binding energies had to be added to the energy values of the internal conversion lines from the radioactive sources in order to get the energies of the nuclear transitions. I studied what had been done in these directions before (*26, 27*), and finally got a feeling that I might make an interesting and perhaps big step forward in this field if I applied the experience I had from nuclear spectroscopy, using the external photoeffect and my high-resolution instruments. Previous investigations had confirmed that the atomic electrons were grouped in shells, and by measuring on the photographic plates the high-energy sides of the extended veils from the various electron distributions, approximate values of the binding energies could be deduced. On the other hand, since the observed electron distributions had no line structure and consequently did not correspond to atomic properties, the precision attained and the actual information were far inferior to what could be obtained by x-ray emission and absorption spectroscopy. I realized that electron spectroscopy for atoms and solids could never become competitive with x-ray emission or absorption spectroscopy unless I was able to achieve such high resolution that really well-defined electron lines were obtained with line widths equal to or close to the atomic levels themselves.

I thought of these problems considerably and started to make plans for new equipment which should fulfill the highest demands on resolution at the low electron energies I had to be concerned with, 10 to 100 times smaller than in radioactive work. I sat down for some days early in 1950 to try to make a thorough calculation of the expected intensities. I designed (*28–30*) an iron-free double focusing spectrometer with $R = 30$ cm, in which I should be able to measure the current with a precision of better than 1 part in 10^4. The spectrometer was surrounded by a big, three-component Helmholtz coil system to eliminate, to better than 1 part in 10^3, the earth's magnetic field over the entire region of the spectrometer. If I had an x-ray tube with $K\alpha$ radiation in the region of 5 keV, this would enable me to measure expelled photoelectrons with a precision of a fraction of an electron volt. This I thought was about sufficient in atomic physics. I also hoped to observe phenomena of chemical interest provided I could realize the resolution I aimed at, but at that time my ideas in this latter respect were of course very vague, centering around atomic level shifts in alloys, and so on.

When I calculated the expected intensities of the photoelectron lines, I started from the very beginning, that is, with a certain number of mA·s in the x-ray tube. I then calculated from existing knowledge the number of $K\alpha$ x-ray photons. Next I put in all solid angles in both the x-ray tube and the electron spectrometer and made some assumptions about the effective photoelectron cross sections to expel electrons from the outermost layers in a solid surface. Those electrons could not be expected to suffer much energy loss and were the interesting ones on which I should base my spectroscopy. In retrospect, this last stage in my considerations was of some interest, in view of the later development of electron spectroscopy into a surface spectroscopy. I guessed that what is now called the escape depth of the electrons should be less than a light wavelength and more than a few atomic layers, and so I used 100 angstroms in my calculations. This was not too bad a guess; later studies indicated a lower figure for metals and 100 Å for organic multilayers. I finally arrived at an estimated counting rate on a photoline in my apparatus of several thousands of electrons per minute as recorded in the Geiger-Müller (GM) counter placed at the focal plane in the double focusing spectrometer. Afterwards I found that this calculation corresponded fairly well to reality. This step, however, took several years to make.

The equipment which I had to build and test was at that time very complicated. The resolution ultimately achieved turned out to be high enough to enable recording even of the inherent widths of internal conversion lines (*24*). This was done in 1954, and in 1956 Edvarson and I published (*31*) an account of this phase of the work under the title "β-Ray spectroscopy in the precision range of 1 : 10^5." In the next phase I had, however, to overcome many difficulties in handling the low-energy electrons excited by x-rays and to record them by the GM counter. This had an extremely thin window through which gas diffused continuously and so was compensated for by an automatic gas inlet arrangement. I did not realize, to start with, the precautions I had to take when dealing with surfaces of solids in order to record resolved line structures.

After some further testing of the equipment, concerning the influence of the finite nuclear size on the conversion lines in some nuclei (*32, 33*), Nordling and Sokolowski and I finally made the transition to atomic physics and recorded our first photoelectron spectrum (*34, 35*) with extremely sharp lines and with the expected intensities. These electron lines had all the qualities which I had set as my first goal. They were symmetric, well defined, and had line widths which could be deduced from the line width of the x-ray line used and the width of the atomic level of the element under study, plus of course a small additional broadening due to the resolution of the instrument. Figure 1 shows an early recording of MgO. The exact position of the peak of the electron lines could be measured with considerable accuracy. Electron spectroscopy for atoms could be developed further with confidence.

Figure 2 illustrates the steps which we took from the earlier recording of the photoelectrons expelled from a gold foil by Robinson (*36*) in 1925 to the introduction of electron line spectroscopy in 1957. The dashed line inserted in Robinson's spectrum should correspond to the place where our spin doublet $N_{VI}N_{VII}$ to the right in Fig. 2 is situated. The distance between the two well-resolved lines in our spectrum would correspond to about 0.1 mm on the scale of Robinson's spectrum. Below this spectrum the black portion has been enlarged (gray scale) to show the corresponding part in our spectrum. This spectrum was taken at a later stage of our development. Within this enlarged spectrum a further enlargement of the $N_{VI}N_{VII}$ doublet is inserted. The spin-orbit doublet now has a distance between the lines which corresponds to a magnification of 600 times the scale in Robinson's photographic recording.

A comparison of the spectra in Fig. 2, b and c, further demonstrates the extreme surface sensitivity of electron spectroscopy. The difference between the two spectra is caused by a slight touch of a finger. At the beginning this sensitivity caused us much trouble, but later, when electron spectroscopy was applied as a surface spectroscopy, it turned out to be one of its most important assets.

In 1957 we published some papers (*34, 35, 37*) describing our first results, which really did indicate great potential for the future. We also obtained our first evidences of chemical shifts (*37–42*) for a metal and its oxides and for Auger electron lines. I thought, however, that we should first improve our techniques and explore purely atomic problems until we had achieved a greater knowledge to enable us to progress to molecular problems. We therefore systematically measured atomic binding energies for a great number of elements with much improved accuracy compared to previous methods, in particular x-ray absorption spectroscopy (*40, 41, 43–61*). We were surprised to find how inaccurate previously accepted electron binding energies for various shells and elements could be. We made so-called modified Moseley diagrams. We were bothered by uncertainties due to the chemical state and therefore tried to use only metals or at least similar compounds of the elements in our systematic studies. We also devoted much effort to the investigation of Auger electron lines (*62–69*), which appeared in our spectra with the same improved resolution as our photoelectron lines. As

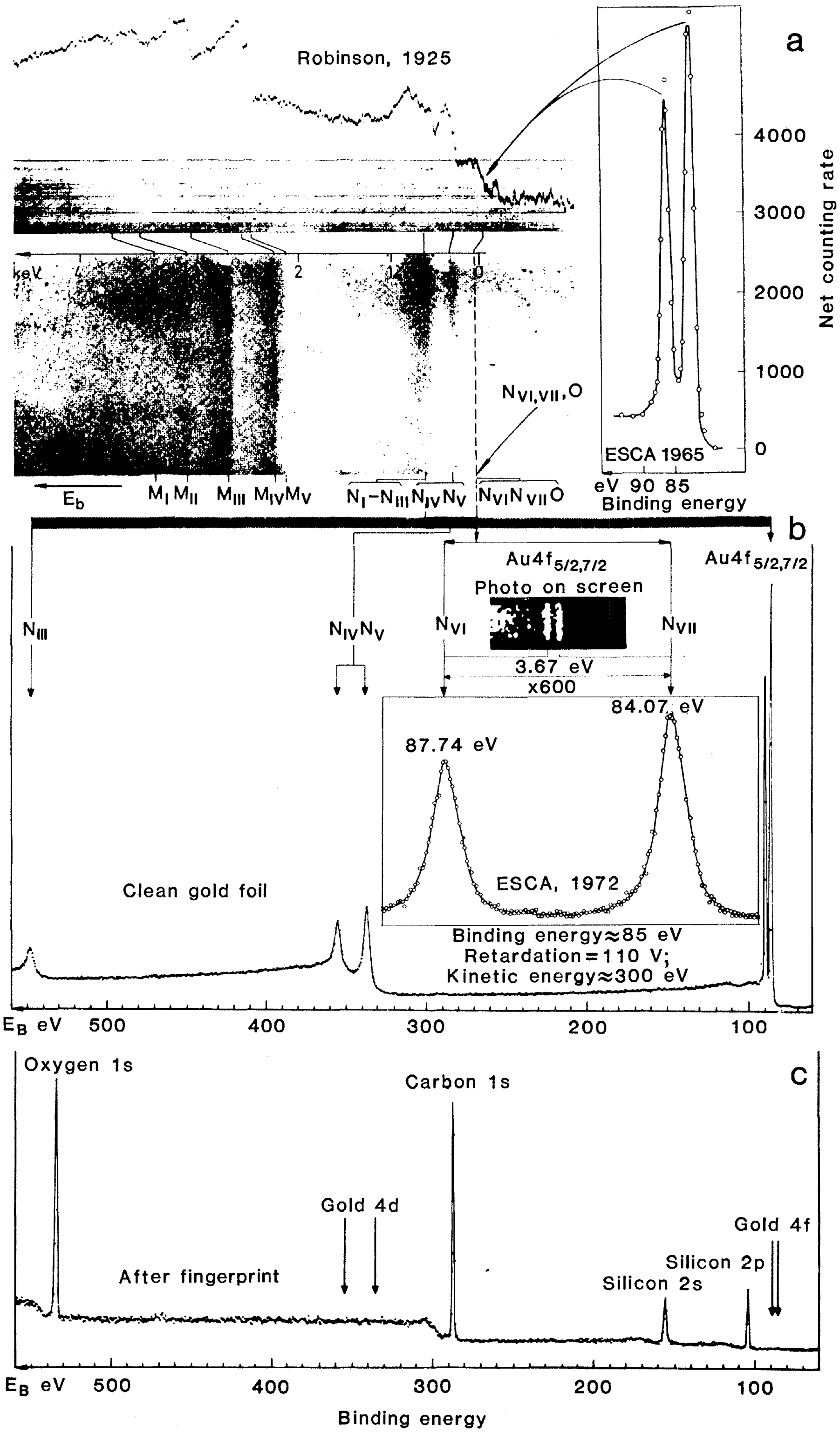
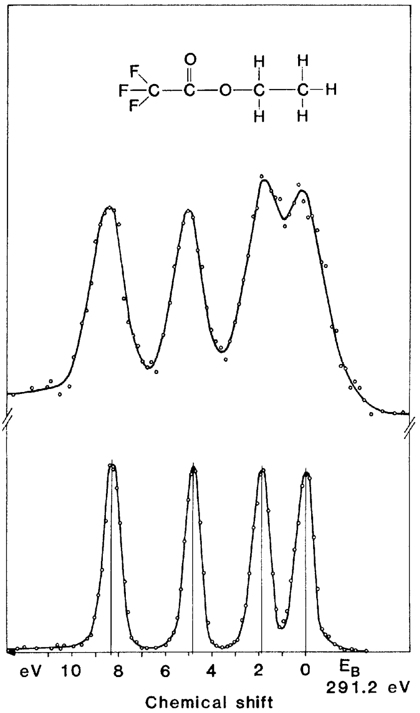


Fig. 2. Electron spectra of gold. (a) At the left is the spectrum recorded by Robinson in 1925 (*36*); at the right, the ESCA spectrum recorded in Uppsala before 1965 by nonmonochromatized Mg$K\alpha$ excitation. The N_{VI} and N_{VII} levels are seen as two completely resolved lines in this spectrum, whereas the N_{VI}, N_{VII}, and O levels appear together as a hump in the photometric recording by Robinson and are only barely visible on the photographic plate. (b) ESCA spectrum recorded in Uppsala in 1972 with monochromatized Al$K\alpha$ excitation. The magnification is 600 times that of Robinson's spectrum. (c) ESCA spectrum of a gold foil with a fingerprint on the surface. The electron lines are entirely due to the fingerprint; the golds lines are missing.

one of the results of such studies we were able to observe, for a group of elements around atomic number $Z = 40$, all the nine lines expected in the intermediate coupling theory as compared to the observed six lines in pure *j-j* coupling (*63*). In general, in the spectroscopy we developed, photoelectron and Auger electron lines were found side by side. Later, therefore, we avoided any notation for this spectroscopy which could give the false impression that only one of the two types of electron lines was present. Auger electron lines can, in addition to the x-ray mode of excitation, be produced by electrons. Much of this basic work on atomic energy levels is described in theses by Sokolowski (*70*), Nordling (*71*), Bergvall (*72*), Hörnfeldt (*73*), Hagström (*74*), and Fahlman (*75*).



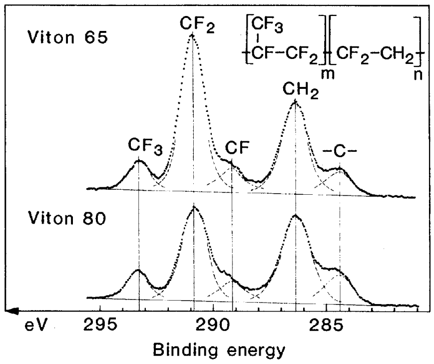


Fig. 3 (left). ESCA shifts of C 1*s* in ethyl trifluoroacetate. Upper spectrum taken without and lower spectrum taken with x-ray monochromatization (*84*, *85*). Fig. 4 (right). ESCA spectra of Viton 65 and Viton 80 polymers.

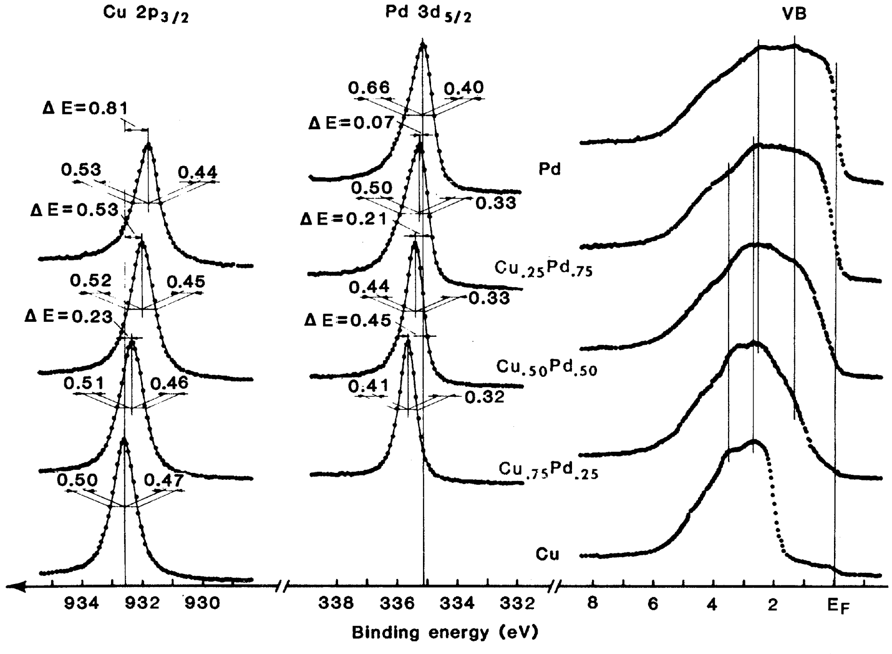


Fig. 5. Core and valence electron spectra (excited by monochromatized Al*K*α radiation) of some Cu_xPd_{1-x} alloys and the pure constituents. Binding energies undergo positive chemical shifts with increasing Cu content. The asymmetries of the lines are due to creation of soft electron-hole pairs at the Fermi edge upon core ionization. The magnitude of the asymmetry is thus related to the (local) density of states at the Fermi level. The Pd lines become more symmetric as the Cu content increases (Pd local density of states decreases).

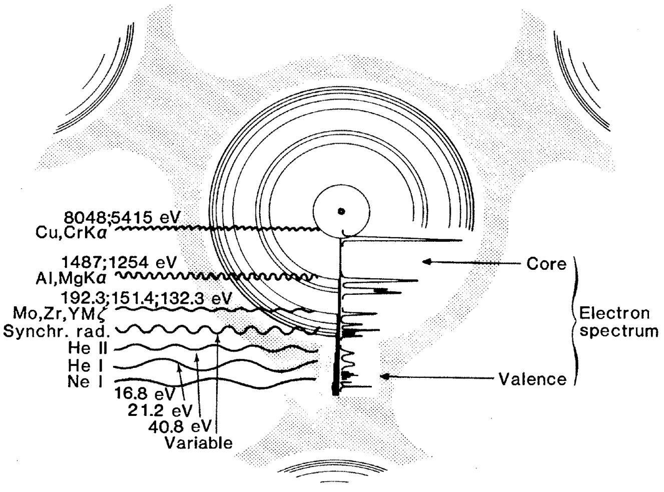
Chemical Shift Effect

After some years' work in electron spectroscopy on problems in atomic physics, the next step came, namely, to make systematic studies of chemical binding. This step was taken with Hagström and Nordling when $Na_2S_2O_3$ was found to give two well-resolved *K* photoelectron lines from sulfur (*76*). This showed that two differently bonded sulfur atoms could be separated in the molecule, which according to classical chemistry were in the −2 and +6 valence states, respectively. This was a more clear-cut case than the copper–copper oxide case we had studied before, since the reference level for the two sulfur atoms could be traced to the same molecule. The systematic investigation of chemical bonding by means of electron spectroscopy is described in theses by Karlsson (*77*), Nordberg (*78*), Hamrin (*79*), Hedman (*80*), Johansson (*81*), Gelius (*82*), and Lindberg (*83*).

Figure 3 shows the chemically shifted carbon 1*s* spectrum of ethyl trifluoroacetate (*84*, *85*). Figure 4 (*86*) shows how the chemical shift effect can be used to identify groups linked together in branched chains in polymers (*87–90*). The intensities of the lines are correlated to the different branchings in the two Viton polymers.

In interpreting the electron spectra, the first step is to consider the electron structure as "frozen" under the photoelectron emission process. In this approximation the measured electron binding energies can be identified with the Hartree-Fock energy eigenvalues of the orbitals. One then disregards the fact that the remaining electronic structure, after electron emission, is relaxing to a new hole state. This relaxation energy is by no means negligible, and an accurate calculation of the relevant binding energies has to include both the ground state and the hole state energies as the difference between them. Inclusion of relativistic effects in this treatment is essential for inner core ionization and heavier elements (*91*). More recently, methods have been devised to describe photoelectron emission by means of a transition operator which properly accounts for the relaxation process (*92–94*). Various conceptual models complement the computational procedures on an ab initio level.

For chemical shifts in free molecules, it is usually sufficiently accurate to consider only the ground state properties (*95–106*). This is because relaxation energies for a series of similar electronic systems vary only marginally. This can



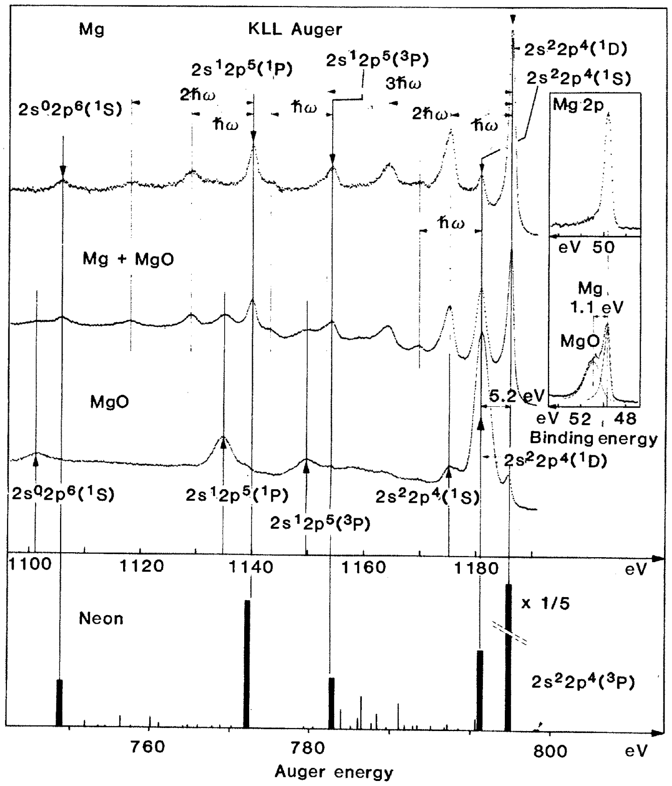


Fig. 6 (left). Regions of binding energies accessible with different photon sources. (Circles) Localized, atom-like orbitals; (shaded area) more or less delocalized, molecular orbitals. Fig. 7 (right). Mg*KLL* Auger electron spectra at different stages of oxidation as obtained in ESCA. The upper spectrum is from a clean metal surface, the lower spectrum from the oxidized metal (with only a trace of metal), and the middle spectrum from an intermediate oxidation. Volume plasmon lines are observed. For comparison, the positions of the Ne*KLL* Auger electron lines are given below, as recorded in the ESCA instrument by means of electron beam excitation.

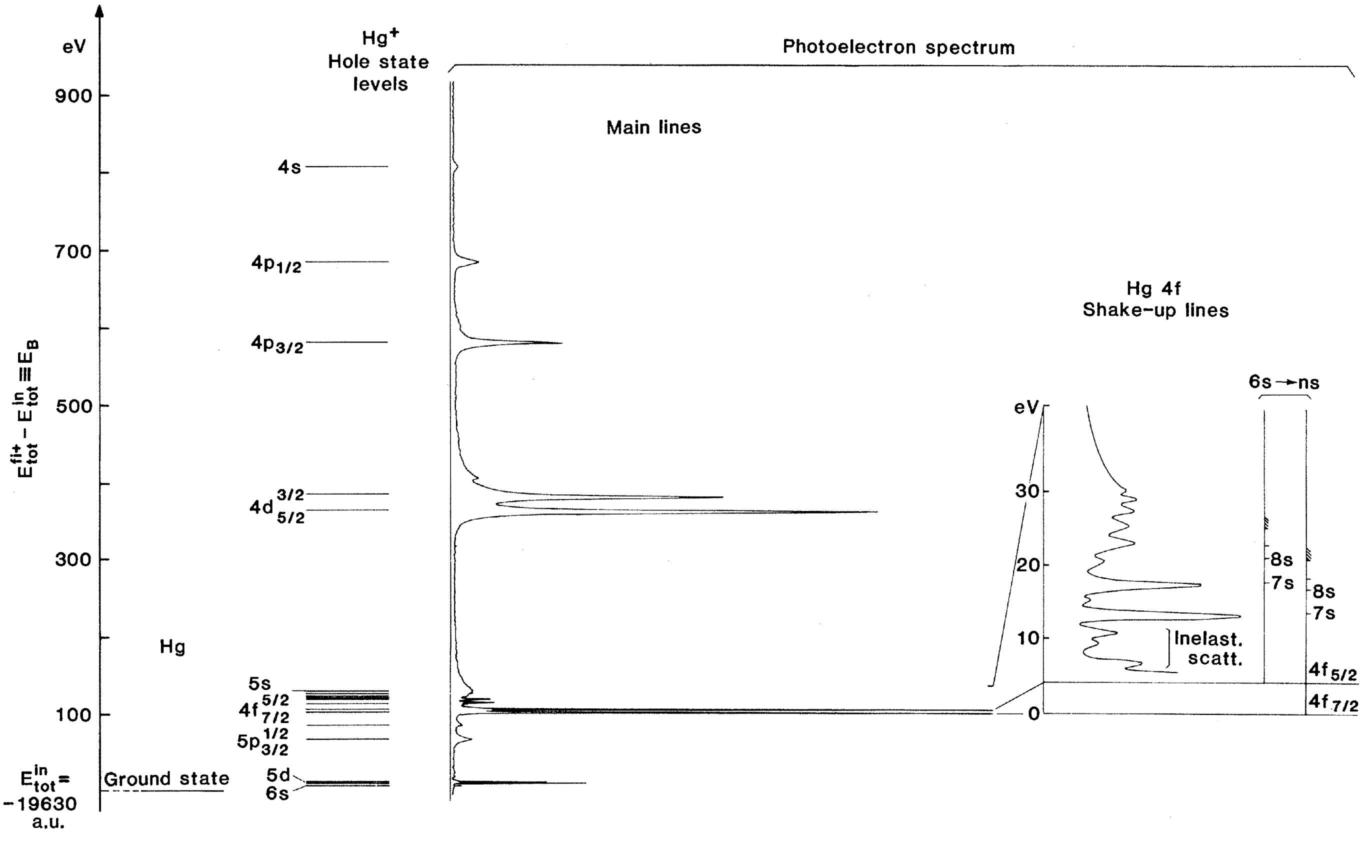


Fig. 8. Relation between hole-state level system and observed photoelectron spectrum for the mercury atom. The main lines are connected with states of the ion where (in a one-electron picture) an atomic orbital has been removed from the neutral ground state. The energy region close to the 4*f* lines is expanded (far right) to show that the additional satellite lines observed (shake-up lines) are due to excitations (6*s*→*ns*) above the 4*f* hole ground states. (Note that the intensities of the 4*f* lines have been truncated to fall into the scale of the figure.) [From (*114*) and (*260*)]

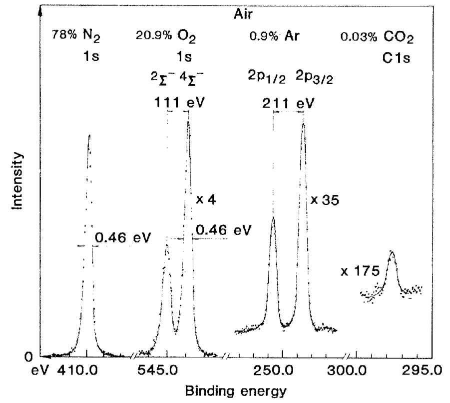


Fig. 9. Electron spectrum of air. The O 1*s* line is split into two components due to spin or multiplet splitting. Excitation was performed with monochromatized Al*K*α ($\Delta h\nu = 0.2$ eV) radiation.

be described by division of the relaxation energy into two contributions, one connected to the atomic contraction at ionization, the other to the "flow" of charge from the rest of the molecule (*107, 108*). The atomic part, which is nearly constant for a specific element, is the dominating contribution to the relaxation energy. The flow part varies generally marginally for free molecules of similar structure, leading to constant relaxation energies. There are cases, however, where the flow part can significantly change from one situation to another. For example, when a molecule is adsorbed on a metal surface, the flow of conduction electrons from the metal substrate will contribute to the relaxation of the core hole. This can increase the relaxation energy by several electron volts (*109, 110*). Other cases are pure metals and alloys, where the conduction electrons are responsible for the screening of the hole (*111–116*). These are treated in theses by Mårtensson (*117*) and Nyholm (*118*).

Electron Spectroscopy for Chemical Analysis

In view of the interesting applications which the chemical shift effect offered for chemistry and the fact that we had found that electron spectroscopy was applicable for the analysis of all elements in the periodic system, we coined the acronym ESCA (electron spectroscopy for chemical analysis). If one is particularly interested in conduction bands for metals or alloys (Fig. 5) (*119*), valence electron structures of solid material in general, or free molecules, more detailed notations may be preferred. One useful distinction is that between core and valence electron spectra (Fig. 6). A further basis of classification is the different origin of the photoelectron and Auger electron lines, which both always occur in ESCA. The corresponding chemical shift effect for the Auger electron lines we established soon afterwards (*69*) in the case of $Na_2S_2O_3$. Further studies (*111, 112, 120–133*) showed that the two shifts effects are complementary. The combination of the two shifts provides insight into the mechanism of relaxation in the photoionization process. Auger electron spectra are shown in Fig. 7 for clean Mg and for the metal when it is partly and finally fully oxidized to MgO (*86*).

Apart from the ordinary core electron lines and the Auger electron lines from the various shells, all characteristic of each element, the electron spectra contain additional features. Satellites situated close to (~ 10 eV) the main core lines at the low-energy sides are often observed with intensities around 10 percent of the latter. Figure 8 (*114*) shows the electron spectrum of gaseous Hg. Inserted are the satellites to the $N_{VI}N_{VII}$ lines. Strong satellites were first observed (*68*) in our spectra in the *KLL* Auger electron spectrum of potassium in some compounds. Satellites have been found to occur frequently for core lines and occasionally have intensities comparable to those of the main lines, for example, in *p*-nitroaniline (*134–136*), transition metal compounds (*137–146*), and various adsorbed molecules on surfaces (*148, 149*). Since these electrons can be visualized as being emitted from excited states, the satellites were given the name "shake-up" lines.

Molecules like O_2 or NO contain unpaired electrons and are therefore paramagnetic. Large classes of solid materials have similar properties. In such cases core electron spectra show typical features called spin, multiplet, or exchange splitting. We first observed this phenomenon (*150*) in oxygen when air was introduced into the gas cell in our ESCA instrument (Fig. 9). The 1*s* line of O_2 is split in the intensity ratio of 2:1. This spin splitting is due to the exchange interaction between the remaining 1*s* electron and the two unpaired electrons in the π_g2p orbital, which are responsible for the paramagnetism of this gas. The resulting spin can be either 1/2 or 3/2. The corresponding electrostatic exchange energies can be calculated and correspond well with the measured splitting of 1.11 eV (*151*). Apart from oxygen and nitrogen, argon and CO_2 can also be seen in air in spite of the low abundances of these gases. A statistical treatment of the data even exhibits the presence of neon (0.001 percent).

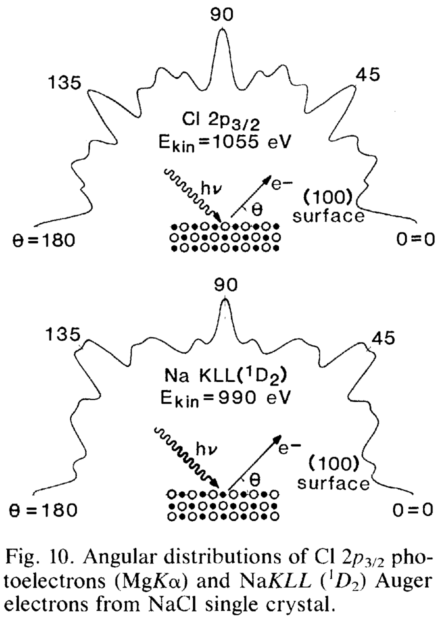


Fig. 10. Angular distributions of Cl $2p_{3/2}$ photoelectrons (Mg*K*α) and Na*KLL* ($^1D_2$) Auger electrons from NaCl single crystal.

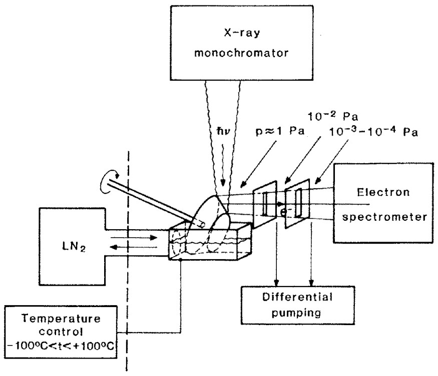
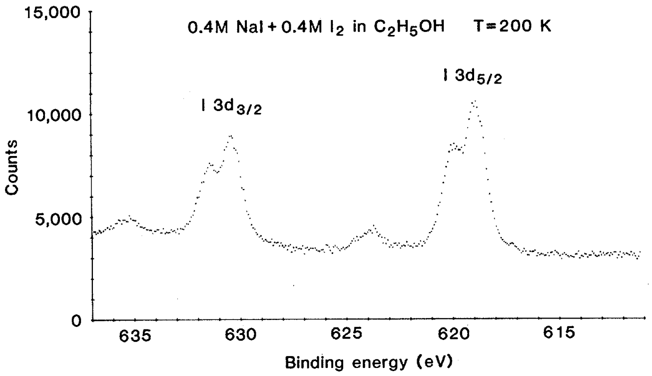


Fig. 11. Schematic diagram of the liquid sample arrangement.

Other features in the spectra occur in the valence electron region, that is, at binding energies extending from zero to say 50 eV. Our first study of this entire region concerned ionic crystals such as the alkali halides (*152*).

In a later study (*153*) of a single crystal of NaCl we discovered the phenomenon of ESCA diffraction. We investigated the angular distribution of emitted Auger electrons from the Na*KLL* ($^1D_2$) transition and the photoelectrons from the Na 1*s*, Na 2*s*, Cl $2p_{3/2}$, and the Cl 3*p* levels, the latter being the outermost valence orbital of the crystal. For excitation both Al*K*α and Mg*K*α were used. The crystal could be set at different angular positions relative to the emission direction of the electrons, which in turn was defined by the slit system of the ESCA instrument. For comparison, the angular distributions from polycrystalline samples were also recorded. In all cases typical diffraction patterns were found. In the control experiments on the polycrystalline sam-



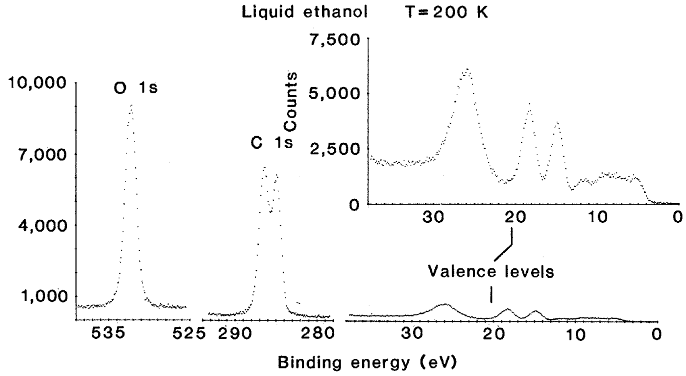


Fig. 12 (left). Iodine $3d$ spectrum from a solution of NaI (0.4*M*) + I_2 (0.4*M*) in ethanol at 200 K. The doublet for each spin-orbit component is due to ionization of the central atom (lower peak) and outer atoms (higher peak) of the I_3^- ion. The extra peaks at the high-binding-energy sides of each spin-orbit component are interpreted as shake-up structures. Fig. 13 (right). ESCA spectrum of liquid ethanol at 200 K.

ples there were no such patterns. Figure 10 shows two of the diffraction patterns recorded. Subsequent measurements (*154–158*) on other single crystals have shown agreement with these results.

ESCA diffraction has more recently been applied to surface studies and gives interesting information on the geometry of adsorbed molecules (*159–161*) on single crystals. This field is under development and should have a promising future in surface science.

In x-ray diffraction there is an incoming photon wave and an outgoing diffracted photon wave. In electron diffraction there is an incoming electron wave and an outgoing diffracted electron wave. In ESCA diffraction there is an incoming photon wave and an outgoing diffracted electron wave with different energies. These are three distinctly different physical phenomena, which require both different types of experimental equipment to observe and different theoretical treatments to evaluate. With instruments built for this purpose and with stronger x-ray sources and synchrotron radiation (*161–164*), the development can proceed further.

In order to study gases and vapors from liquids, we first introduced a freezing technique (*165*) to condense the gases onto the specimen plate. In this way we obtained the valence or molecular orbital spectrum of solidified benzene (*166*). Soon afterward we found that we could study the gaseous phase just as well by introducing differential pumping in the instrument. We first studied acetone with this technique for gases (that is, for free molecules) and found two well-separated C 1*s* core lines, one for the keto carbon and one for the methyl carbon in the intensity ratio of 1:2 (*167*).

Since solids, surfaces, gases, and vapors from liquids were all found to be suitable samples in electron spectroscopy, the question arose whether liquids could also be studied. This turned out to be possible, and several satisfactory methods have been developed in our laboratory (*168–173*). The early methods and applications are described in theses by H. Siegbahn (*174*), Asplund (*175*), and Kelfve (*176*). Recently, a new, more convenient arrangement (H. Siegbahn) has been developed, which is shown in Fig. 11 (*173*). A small trundle rotates in the sample cell, into which the liquid is introduced. A slit transmits the exciting radiation, such as x-radiation, and the electrons expelled from the continuously wetted trundle can leave the housing through a slit, where differential pumping reduces the gas pressure. Sample cooling has been introduced, which has enabled a vast increase of the number of liquids that can be studied. Figure 12 shows part of a recent (*173*) spectrum of ethanol as a solvent in which iodine and sodium iodide are dissolved. A well-resolved spin-orbit doublet of iodine $3d_{5/2}$ and $3d_{3/2}$ is observed. Each of these electron lines is chemically split in the ratio of ~ 1:2. The interpretation is that I_3^- has been formed in the solution. The centrally located iodine has the highest binding energy. The correct intensity ratio of 1:2 is obtained when the shake-up satellites are ascribed to the two externally situated iodine atoms, which is in agreement with what we have found for similar configurations in other electron spectra. The spectrum of liquid ethanol

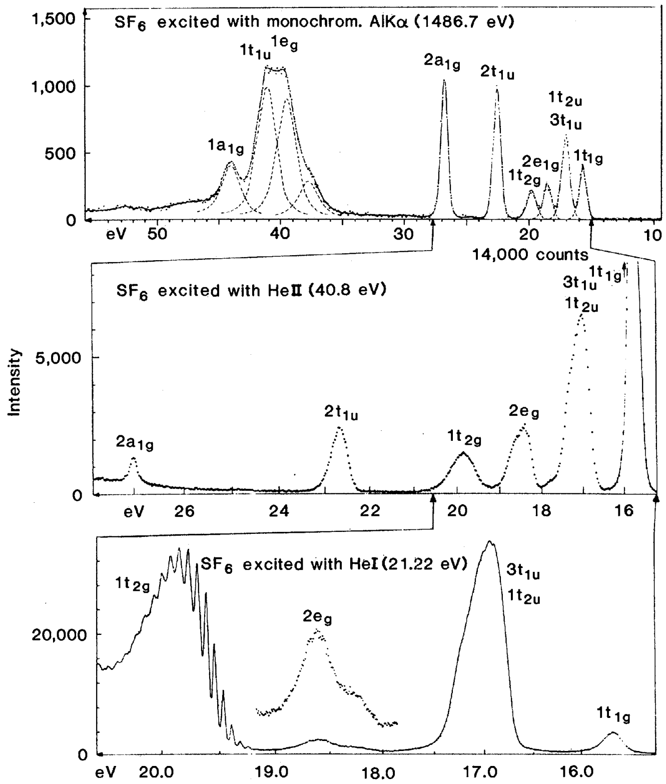


Fig. 14. Valence electron spectra of SF_6 excited with different photon energies (Al*K*α, HeII, and HeI radiation), illustrating the complementary nature of the various excitation sources. The Al*K*α-excited spectrum enables a recording of the full valence region (including the innermost orbitals), which is not possible with the lower photon energies. The higher resolution in the spectra excited with He resonance radiations allows the study of finer details of each of the outer electron bands. Note also the strong variations in the relative intensities of the bands as a function of photon energy. This can be used as an aid in assigning the spectrum (*197, 198*).

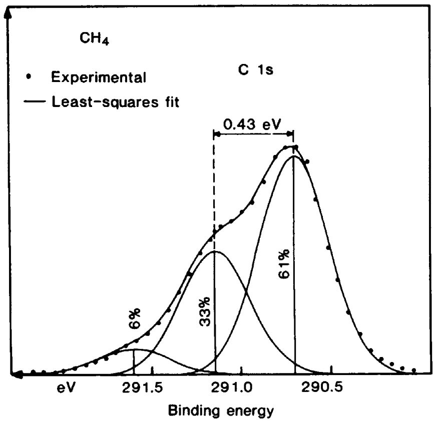


Fig. 15. Vibrational structure of the core electron line C 1*s* in CH_4. The line structure can be quantitatively explained as a consequence of shrinkage of the equilibrium distances on core electron emission (*217*).

is shown in Fig. 13, which shows the oxygen 1*s* core line, the chemically split carbon 1*s* line, and the valence electron spectrum. The field of liquids is in a state of rapid development.

In the valence region for free molecules it was possible to achieve much improved resolution if ultraviolet light, especially He resonance radiation at 21 eV, was used for excitation. Development work in this field was performed by Turner (*177–182*) and Price (*183, 184*) and their co-workers in England. Conduction bands of metals could be studied by a corresponding technique using ultrahigh vacuum (UHV), which was done by Spicer and co-workers (*185–188*) in the United States.

In my laboratory a large electrostatic sector focusing instrument was designed in the early 1960's for excitation of electron spectra in the gaseous phase by vacuum ultraviolet (VUV) radiation and by electrons. High-resolution valence electron spectra were thus obtained, and Auger and autoionization spectra of rare gases and organic molecules could be investigated at a resolution that enabled vibrational structures to appear. Studies of angular distributions were initiated by using polarized radiation. This was produced by VUV polarizers which we developed. Much of this work is described in theses by Bergmark (*189*), Karlsson (*190*), Jadrny (*191*), and Mattsson (*192*). Auger electron spectroscopy was further explored in more recent publications (*128, 132, 193–196*).

The source of excitation was for a time confined to either the soft x-ray region or the ultraviolet region, with a gap between them from ~ 50 eV (HeII) to 1250 eV (Mg*K*α). Figure 14 shows the valence spectrum of SF_6 excited by HeI, HeII, and Al*K*α (*197, 198*). Some intermediate x-ray lines were later added (*199–205*), such as Y*M*ζ at 132 eV, but the main step was the introduction during the 1970's of variable synchrotron radiation (*206–210*), which partly bridged the gap. The previous strong distinction between x-ray- and ultraviolet-excited electron spectra is therefore not so easy to maintain any more unless one is emphasizing a particular technique for exciting the spectra. This is not a trivial point for most researchers, however, and excellent work can be done with one or the other technique alone or in combination.

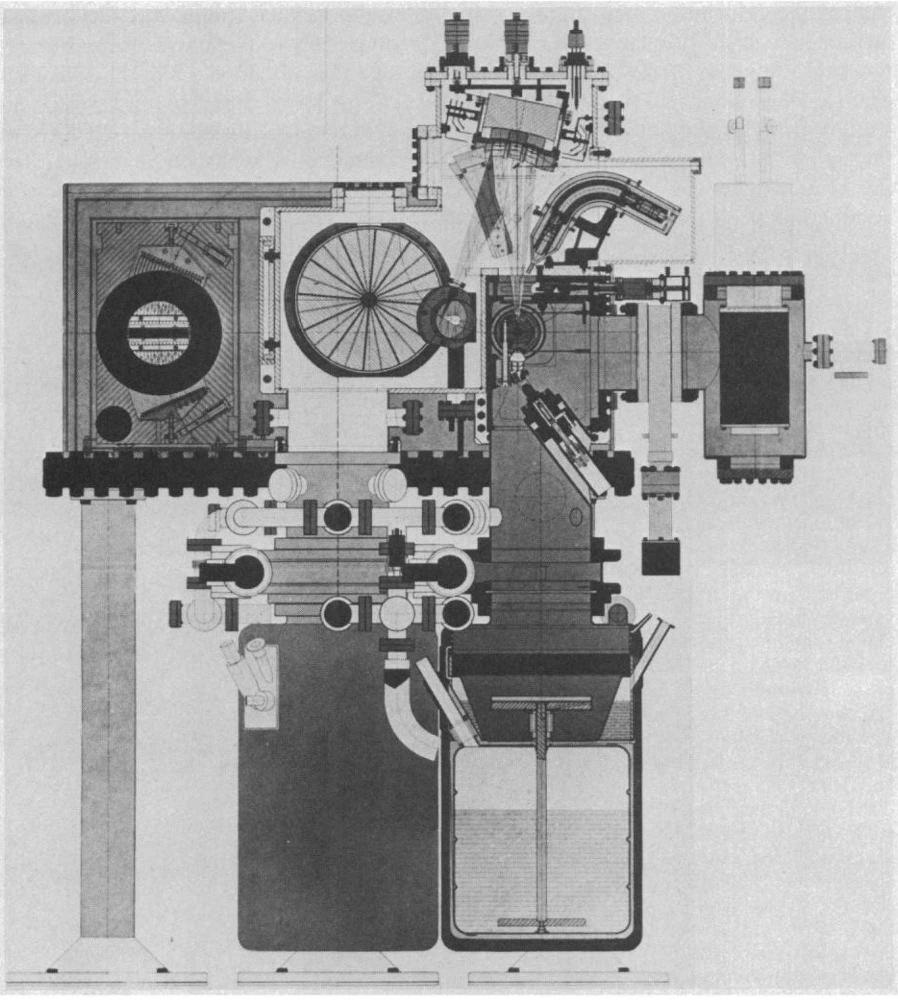


Fig. 16. Side view of the new ESCA instrument for free molecules and condensed matter. The instrument is UHV-compatible and includes four different excitation modes (monochromatized Al*K*α, monochromatized and polarized ultraviolet, electron impact, monochromatized electron impact).

In 1967 we had gone through most of the basic features of the spectroscopy, designed several new spectrometers (electrostatic double focusing ones included), developed new radiation sources in the soft x-ray and ultraviolet region, made theoretical investigations of the process of electronic relaxation at ionization, and applied the spectroscopy to a variety of different research fields. We then decided to present the new spectroscopy in a more consistent and complete way than we had done before. At the end of that year our book *ESCA—Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy* appeared (*211*). Two years later we published a second book, *ESCA Applied to Free Molecules* (*212*). At that time several firms started to develop commercial instruments. I took part in one of these developments at Hewlett-Packard in Palo Alto during a leave of absence from my laboratory in 1968. I spent that year at the Lawrence Berkeley Laboratory, with which we had had a long cooperation in nuclear spectroscopy and then in ESCA. The Hewlett-Packard instrument (*213*) was designed to include a monochromator for the Al*K*α radiation, consisting of three spherically bent quartz crystals and a retarding electrostatic lens system to match the dispersion of these crystals to the electron spectrometer.

The spherically bent quartz crystal

monochromator, which was double focusing, was invented in my laboratory in 1958 (*214*) in another connection, namely, in low-angle scattering of x-rays against latex and other particles of biological interest (*215*). The combination of double focusing both in the x-ray monochromator and in the electron analyzer has turned out to be essential for further progress in ESCA. Other important technical developments have been the introduction of swiftly rotating water-cooled anodes (U. Gelius), multidetector systems with electron channel plates, and computerization of the instruments (E. Basilier).

Development of New Instruments

In 1972 Gelius and I made a new instrument (*85, 216*) with all these components included, particularly designed for studies of gases. With the improved resolution of this instrument new structures could be resolved. Of principal interest was the discovery of the vibrational fine structure of core lines (*82, 217*). Figure 15 shows the line profile of the C 1*s* in CH_4. It turns out that this line can be separated into three components caused by symmetric vibration when photoionization occurs in the 1*s* level of the central carbon atom. When the photoelectron leaves the methane molecule the latter shrinks about 0.05 Å. The minimum of the new potential curve for the ion will consequently be displaced by the corresponding amount, and Franck-Condon transitions which take place will then give rise to the observed vibrational fine structure of the electron line with the intensities given by the Franck-Condon factors. This finding can be correlated with our simultaneous discovery of vibrational fine structures in soft x-ray emission lines (*218–233*). This development is further described in theses by Werme (*234*), Nordgren (*235*), and Ågren (*236*). Combined, these results show that vibrations occur in these molecules during x-ray emission in both the initial and the final states.

The high-resolution instrument designed with Gelius was planned to be a prototype for a new generation of advanced instruments, which have now been constructed in a laboratory for electron spectroscopy recently built in Uppsala (*237*). These have just been finished and are the sixth generation in the sequence from my laboratory since 1954. Two of the new instruments are designed for molecular studies and the third for surface studies. The spherical electrostatic analyzer (R = 36 cm) is provided with an electrostatic lens system due to Wannberg (*238*). The modes of excitation included in the instruments are monochromatic Al$K\alpha$ radiation ($\Delta h\nu$ = 0.2 eV) at 1486.6 eV, an ultraviolet light source with a grating providing selected lines between 10 and ~ 50 eV, an electron monochromator of variable energy with an energy homogeneity of $\lesssim$ 10 meV, and an additional electron gun for Auger electron excitation, also variable in energy (Fig. 16). A polarizer for the ultraviolet light at different wavelengths can be used in angular distribution studies.

The brief account I have given concerns the work done in my laboratory in the development of electron spectroscopy. During the 1970's several reviews and books on electron spectroscopy were written, and for a complete account the reader should go to such sources (*239–258*). Two new books from my laboratory by H. Siegbahn and Karlsson (*259, 260*) cover the developments mainly after 1970 and present current experimental and theoretical aspects of electron spectroscopy.

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Cardiovascular Research: Decades of Progress, a Decade of Promise

Robert I. Levy and Jay Moskowitz

Summary. Mortality due to cardiovascular diseases has decreased more than 30 percent in the last 30 years, and this decline has accelerated so much that over 60 percent of it has occurred between 1970 and 1980. The past and present contributions of advances in cardiovascular research to this decline are reviewed. Although there have been significant research accomplishments, too many people still die of heart and blood vessel diseases. Continued emphasis must be placed on research in the areas of etiology and pathogenesis, on validating potentially beneficial research hypotheses, and on the translation and dissemination of research results to the health care practitioner and the public. Only then can our long-term goal, the prevention of cardiovascular disease, be fully realized.

Heart and blood vessel diseases have been the major cause of death in the United States for more than 40 years and account for over half of all deaths (Fig. 1). The magnitude of the health care problem caused by these diseases cannot be overemphasized. Each day, an estimated 3400 Americans, more than two each minute, suffer a heart attack (*1, 2*). Each day, approximately 1600 people suffer strokes. Some 25,000 children are born with defective hearts every year, and there are over 100,000 children and 1.7 million adults who suffer from rheumatic heart disease (*1–3*).

The leading cause of death in the United States is coronary heart disease, which accounts for two-thirds of all cardiovascular deaths. It alone was responsible for nearly 650,000 deaths in 1978, and more than 150,000 of these occurred in people less than 65 years old. Approximately one-third of the deaths from all causes in persons between the ages of 35 and 64 years are due to coronary heart disease, and nearly 40 percent of all deaths in white males aged 55 years and over are caused by this disease (*4*). In contrast, all forms of cancer combined (the second leading cause of death) were responsible for nearly 400,000 deaths in the United States in 1978 (*5*). Cardiovascular diseases have led the list of the nation's killers for more than half a century, and they remain so today despite a steady decline in heart disease death rates since the 1950's (Fig. 2). The social and economic toll of diseases of the heart and blood is equally severe. In fact, cardiovascular disease accounts for more bed days than any other single condition. The total economic cost of cardiovascular disorders is estimated to be in excess of $60 billion annually (*6*). Of this amount, $20 billion represents health expenditures, $10 billion productivity lost due to illness, and $30 billion potential productivity lost due to early death (*6*). This $60 billion accounts for more than one-fifth of the total cost of illness in the United States.

Magnitude of Decline in Mortality from Cardiovascular Diseases

Cardiovascular mortality has decreased more than 30 percent in the last 30 years, and this decline has accelerated so much that over 60 percent of it has occurred between 1970 and 1980 (*5*) (Fig. 2). Among people between 25 and 44 years of age, deaths as a result of heart disease have declined from first to third

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