Electron Spectroscopy for Chemical Analysis (E.S.C.A.)

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Electron spectroscopy for chemical analysis (e.s.c.a.)

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INTRODUCTION

The electronic structure of matter has so far been studied almost exclusively by means of the electromagnetic radiation which is being emitted (or absorbed) at excitation. Apart from some early attempts, the electrons themselves were not directly detected. The various energy levels which could be studied by different modes of excitations were observed as photons being emitted (or absorbed) when electrons were making quantum jumps between two levels. Over a long period of time spectroscopy in the visible, infrared, ultraviolet, and X-ray parts of the electromagnetic spectrum was gradually perfected and extensively used in many kinds of applications. More recently, other and in some cases more sophisticated techniques, like n.m.r., e.p.r. and microwave spectroscopy, have been added to previously existing spectroscopic tools.

During the last decade serious attempts have been made to explore the possibility of developing a spectroscopy based on the direct observation of the electrons. The results are encouraging. Despite many initial experimental difficulties it now seems evident that these can be solved in a surprisingly satisfactory way. Moreover, new types of information have become accessible and the fields of application are numerous. In the following I will give a brief account of some of the work which my group at Uppsala has performed and which is largely covered by the book *ESCA—Atomic, molecular and solid state structure studied by means of electron spectroscopy*. More recently our group has published a second book entitled *ESCA applied to free molecules*, dealing exclusively with gases.

MODES OF EXCITATION

There are essentially three ways to excite electron spectra as shown in figure 1, namely by X-rays (particularly soft X-rays), u.v. light, or electrons (ions). We have used all three methods but most of our work concerns soft X-rays. There are advantages and also limitations attached to each technique. The reason why we have made preference to X-ray excitation is the fact that all (internal) atomic and (external) molecular levels can be excited by this radiation and furthermore that not only gases but also solid material can be conveniently studied. U.v. excitation has the advantage that electron lines with much less inherent widths can be obtained because of the less inherent widths of the u.v. lines. The technique is limited to the external part of the molecular orbitals (usually $E_{\text{binding}} < 30$ eV). Deeper orbitals and also the specific chemical shifts of the individual atomic levels associated with the atomic charge distribution within the molecules cannot be observed. The technique is also mainly limited to gases, although information about solid state band structure can be obtained under conditions of extreme vacuum and with special precautions as to the surface conditions. Electron excitation, finally, is useful for gases to explore Auger and autoionization electron spectra. Higher intensities are obtained by this mode of excitation than by X-ray excitation, but it is destructive for most solid compounds and can of course not produce ordinary photoelectron lines.

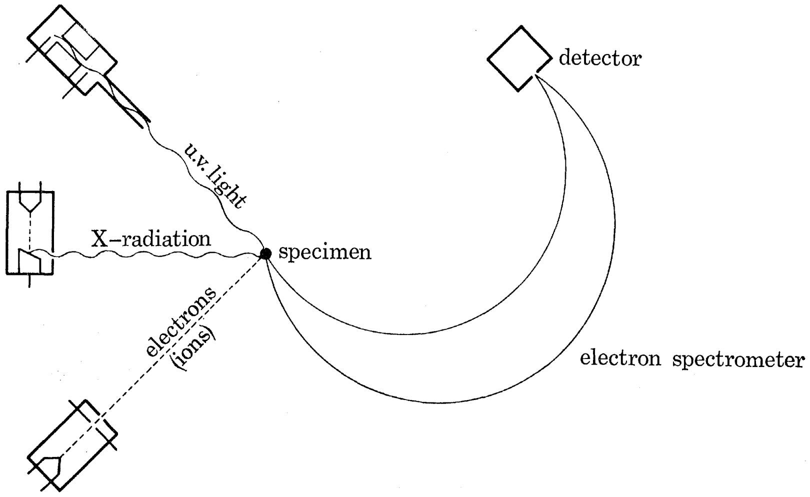


FIGURE 1. Three different modes of excitation of electron spectra.

SOME GENERAL FEATURES

Figure 2 is a comparison between the well-known X-ray emission lines Kα_1 and Kα_2 from Cu and the corresponding L_{III} and L_{II} e.s.c.a. lines using MgKα for the excitation. The K$\alpha_1\alpha_2$ X-ray doublet was recorded at highest possible resolution and represents consequently the inherent line widths. As can be observed the e.s.c.a. lines are still sharper, the reason being the smaller inherent width of the MgKα excitation line compared to the broader K level in Cu which is involved in the X-ray transitions from the L_{III} and L_{II} levels to that level. It turns out that it is always possible to find one or several narrow atomic levels for any element in the Periodic System which can conveniently be excited by MgKα or AlKα radiation. If, for some reason, still deeper atomic levels are to be exicted other X-ray lines can be used, e.g. the Kα lines of Cr, Cu, Ag, or W. For most work in molecular or solid state physics Mg or Al X-ray excitation is adequate and even preferable because of the relatively small inherent width (about 0.7 eV and 0.9 eV, respectively).

Figure 3 shows an e.s.c.a. spectrum of Au (MgKα excitation) with the N_{VI}, N_{VII} spin doublet as prominent lines. The MgK$\alpha_{3,4}$ satellite lines also give rise to e.s.c.a. lines for the same levels. At binding energies near zero the Au conduction band electron distribution is also recorded. Similar conduction band spectra have now been studied for many elements and also some alloys. For precise work heating of the samples (in some cases also by using hydrogen at low pressure for reduction) has turned out to produce clean surfaces. Surface oxidation or surface contamination by carbon can be removed in this way, the result being possible to follow closely in the e.s.c.a. spectrum by means of the oxygen or metal oxide lines or, alternatively, the carbon line. Plasmon electron lines are also visible (see figure 4).

From an analytical point of view it is interesting to note that e.s.c.a. is applicable over the entire Periodic System, including the light elements like carbon, oxygen, and nitrogen. Also beryllium, lithium, and even helium have been studied and at the other end of the Periodic System transuranic elements can be observed in minute quantities. In this connexion it is of interest to know something about the sensitivity of the method. In order to study this question a series of multimolecular layers of stearic acid on a metal backing was prepared with an iodine atom substituted at the end of each molecule. By observing the e.s.c.a. spectrum for iodine at different thicknesses of the layers it was found that e.s.c.a. lines are effectively produced from a surface layer of around 100 Å. Electrons produced much below this depth in the sample suffer energy losses and are thrown out from the e.s.c.a. line. These electrons eventually contribute to the background under the lines. The sensitivity is such that less than an atomic monolayer of an element of the surface gives a measurable e.s.c.a. line.

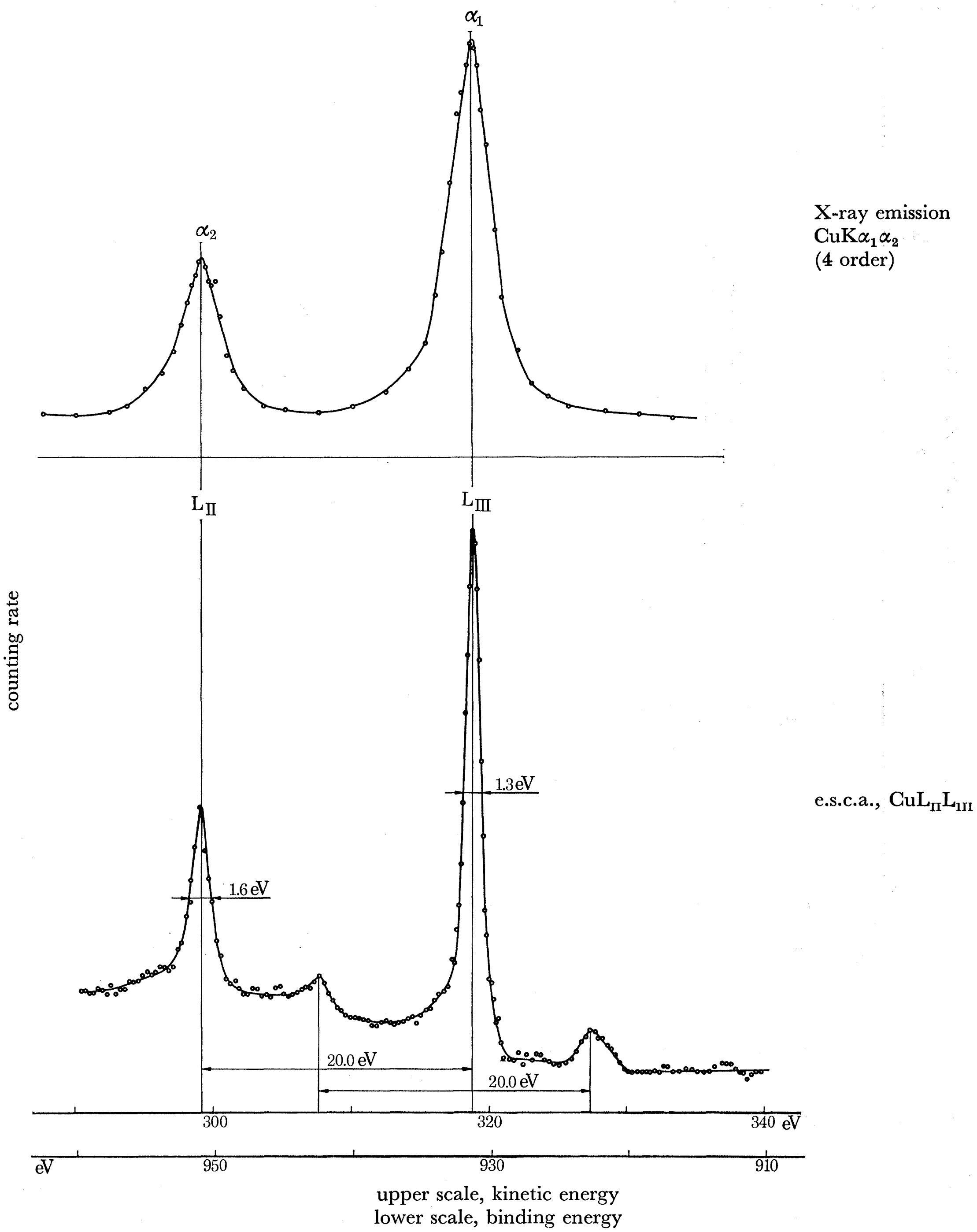


Figure 2. Comparison between X-ray emission lines Cu ($K\alpha_2 + K\alpha_1$) and the corresponding e.s.c.a. lines Cu ($L_{II} + L_{III}$).

The e.s.c.a. lines have a width which, also for solid samples, is set by the inherent width of the exciting X-ray line and the inherent width of the level under study. The spectrometer aberration has been reduced to the extent that it contributes very little to the observed e.s.c.a. line widths. The inherent width of the 1s level of carbon is of course of particular interest to know since this would be the ultimate limit of resolution at e.s.c.a. studies in organic chemistry provided that the influence of the exciting X-ray line width could be eliminated. In the case of CO in gaseous form (see figure 24) we have recently been able to observe vibrational structure in both the Auger electron spectrum and the autoionization electron spectrum. The vibrational line components are clearly resolved from each other at a distance of some 0.15 eV. Since the 1s level in carbon is involved in these transitions this level width must be smaller than 0.15 eV.

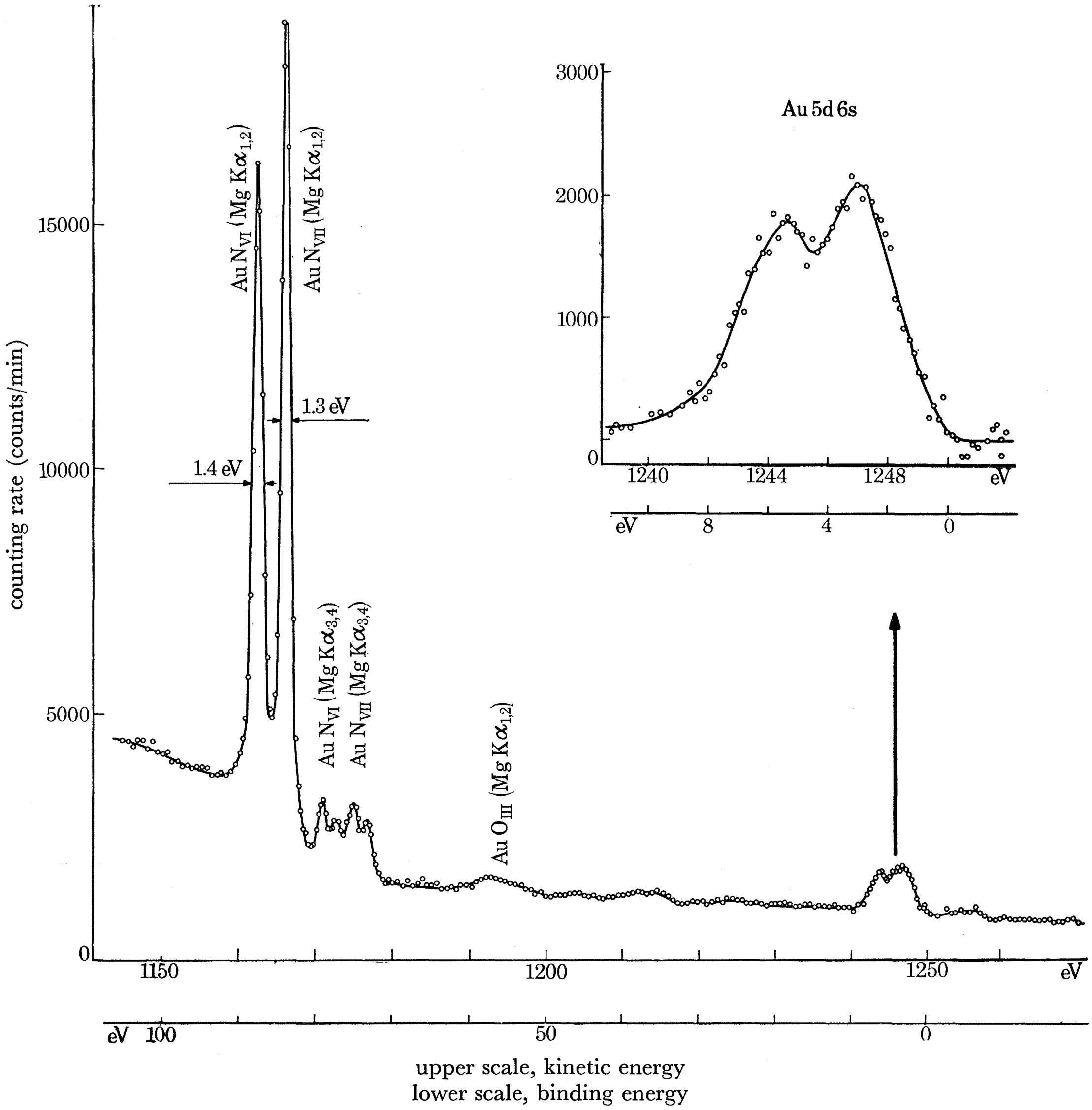


Figure 3. E.s.c.a. spectrum of the outer levels of gold. The conduction band of gold is displayed separately.

There is some hope to partially eliminate the contribution from the inherent line width of the exciting X-radiation by means of crystal monochromatization. Two different schemes to achieve this are presently under development. One of the schemes is discussed in our first book on e.s.c.a. (see References) and is based on a concept called 'dispersion compensation'. The X-ray line is dispersed along the sample surface and by a proper balancing of the crystal dispersion and the electron spectrometer dispersion a compensation of the inherent X-ray line width can in principle be achieved. The second scheme is illustrated in figure 5. A high intensity electron

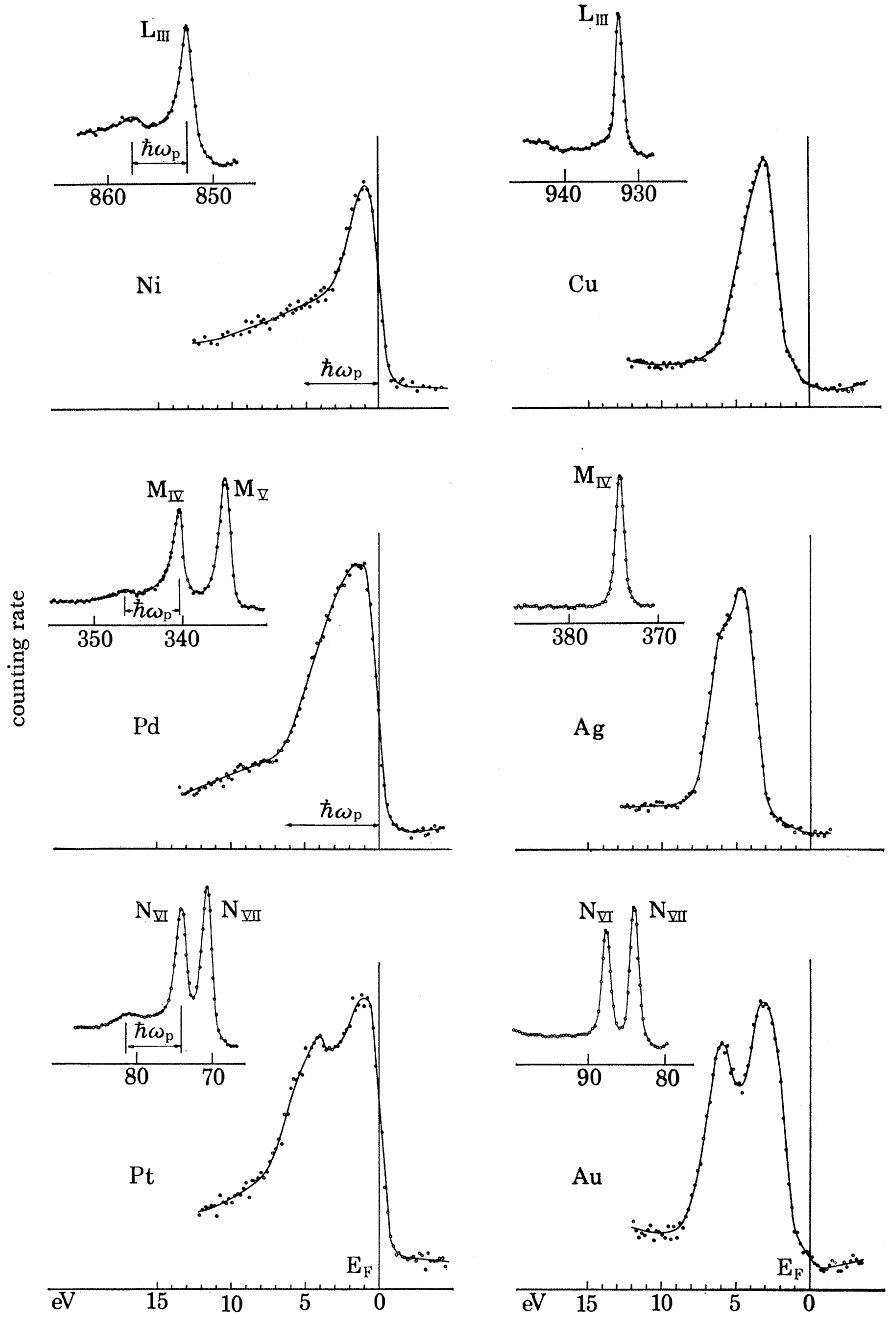


FIGURE 4. Conduction bands of the metals of Group I*b* and the metals Ni, Pd and Pt in Group VIII. These metals have d and s symmetry bands with the s part extending to higher energies. The main contribution to the spectrum comes form the d electrons. The metals in Group VIII have one electron less in the conduction band and the Fermi energy is shifted correspondingly in the e.s.c.a. spectra. Core electron lines are inserted in the figure for each of the metals. Satellite lines due to plasmon energy losses ($\hbar w_p$) are observed.

gun produces a small focal spot on the periphery of a rotating aluminium anode. A spherically bent quartz crystal diffracts the AlKα line and forms a focus on the Rowland circle at the entrance slit of the electron spectrometer (either a magnetic or an electrostatic instrument). With a sufficiently concentrated size of the electron beam focal spot the beam power can be effectively used to give a diffracted X-ray beam image with a width which is less than the natural width of the Kα line of aluminium. This scheme would be well suited for e.s.c.a. studies of gases at high resolution and of course also of solid material.

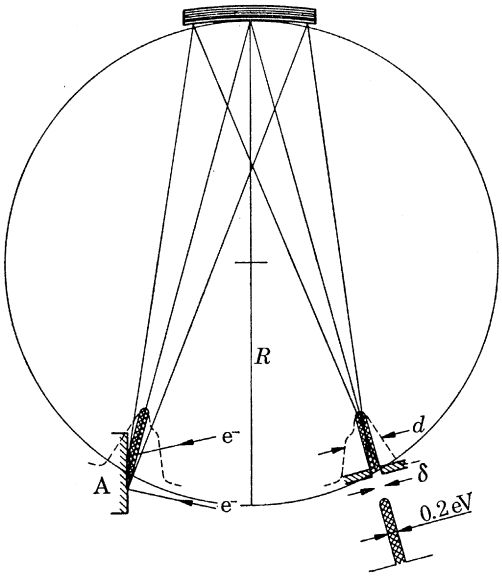


FIGURE 5. Scheme to achieve e.s.c.a. lines having widths less than the inherent width of the exciting X-rays.

SOME APPLICATIONS

I will give some examples of e.s.c.a. spectra to elucidate some kinds of applications. Figures 6 and 7 show the vitamin B_{12} structure and part of the corresponding e.s.c.a. spectrum. The fact that a single Co atom can easily be observed within this big molecule indicates the potentialities of e.s.c.a. to deal with problems in biochemistry. Another example is given by insulin. This molecule consists of 51 amino acids with three disulphide bridges, two of which bind the two peptide chains together. Sulphur in this biomolecule can be recorded in the e.s.c.a. spectrum and the splitting of the two chains by chemical treatments can be observed in the e.s.c.a. spectrum as a splitting of the sulphur line in two separate lines because of the 'chemical shift' effect. More recently we have been able to record both the sulphur and even the iron electron line in the enzyme cytochrome *c*. This biomolecule occurs in all aerobic cells and takes part in the metabolism as a link in the oxidation chain transporting electrons between the substrate and oxygen. Its molecular mass is 12700 and it has a structure with a haem group covalently attached to it. It contains only four sulphur atoms and one single iron atom. When the enzyme transports the electrons the ion valence is changing between +2 and +3. The specific role of such biologically active metal ions (Mg, Fe, Cu, Zn, etc.) in the large biomolecules is well recognized in biochemistry, and our preliminary results indicate that studies of such properties of metal ions may be within the reach of e.s.c.a.

The chemical shift effect can be described in the following way: it is related to the changes

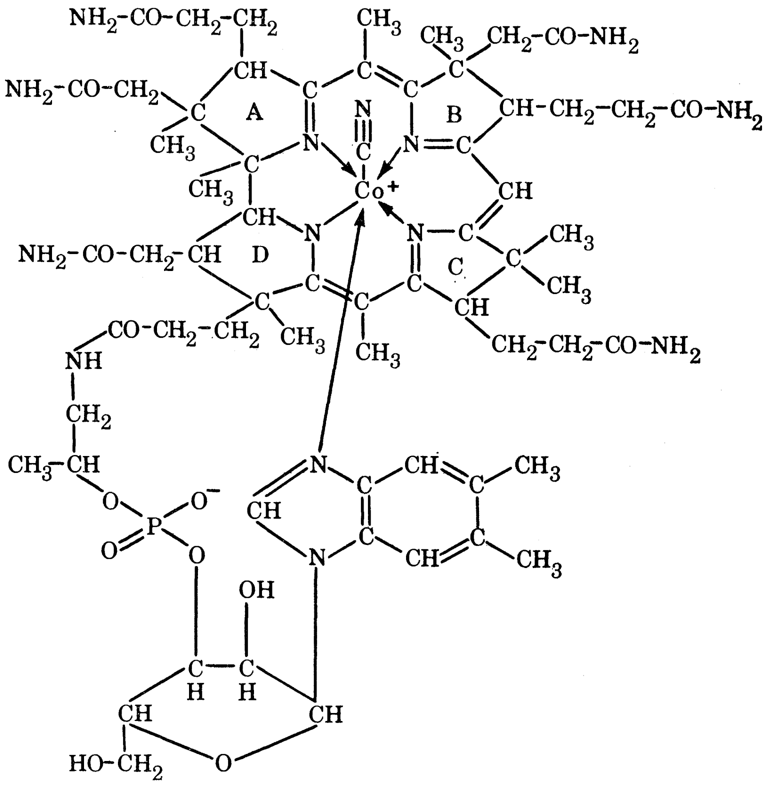


FIGURE 6. The vitamin B_{12} molecule. One cobalt atom among 180 atoms of other elements.

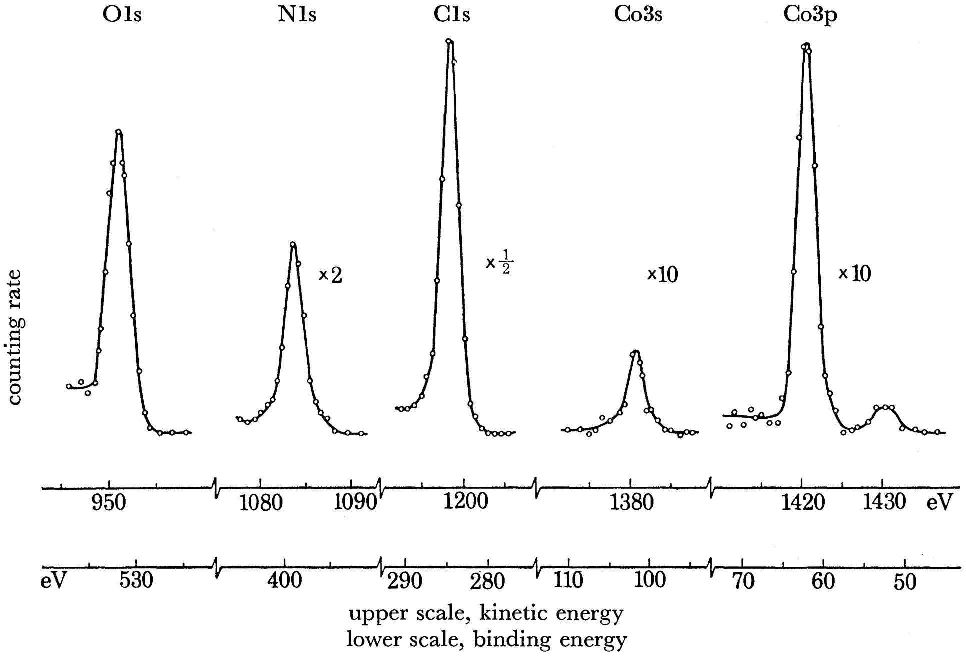
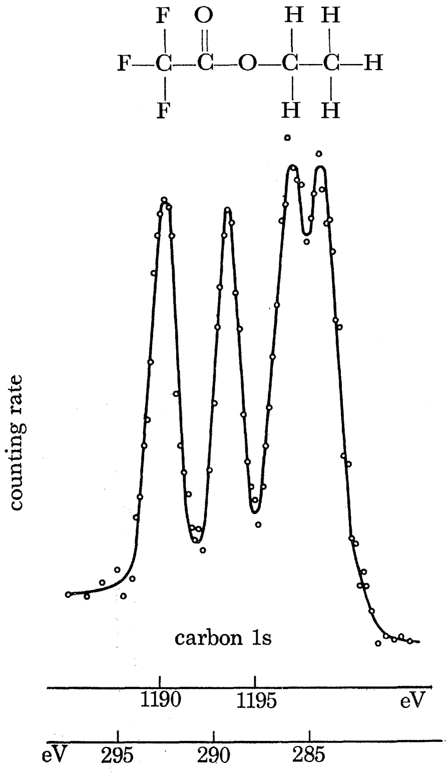


FIGURE 7. Electron spectrum from vitamin B_{12} with lines from oxygen, nitrogen, carbon and cobalt.

that occur in the core electron spectra of atoms in different chemical environments. The change in wavefunction that occurs for the outer electrons usually means a displacement of electric charge in the valence shell so that the interaction between valence electrons and core electrons is changed. Thus a change in chemical (or crystallographic) environment of an atom is relayed to the core electrons and induces a slight change in their binding energies. These chemical shifts of the inner electron energies can now be measured by electron spectroscopy and are likely to assist in the solution of many problems in chemistry, like molecular charge distributions and chemical bonding. A particular feature of e.s.c.a. is thus that one obtains information on chemical and molecular dynamics by measuring a quantity that remains essentially atomic in character. Thus one can move the area of inspection from one atomic species to the other in the molecular structure.



upper scale, kinetic energy
lower scale, binding energy

FIGURE 8. Electron spectrum from carbon in ethyl trifluoroacetate.

FIGURE 9. Nitrogen 1s electron spectrum from sodium azide.

A typical chemical shift spectrum is given in figure 8, showing carbon in ethyl trifluoroacetate. All four carbon atoms in this molecule are distinguished in the spectrum. The lines appear in the same order from left to right as do the corresponding carbon atoms in the structure that has been drawn in the figure.

Figure 9 is an example of the chemical shift of nitrogen in sodium azide. The peaks corresponding to the positively and negatively charged nitrogen atoms are identified from the line intensities (1:2). Figure 10 shows how two nitrogen atoms differently situated in a bigger molecule, 3-nitrobenzene sulphonamide, can be distinguished from each other because of the chemical shift effect.

In the application of e.s.c.a. to chemical problems, it is desirable to be able to explain the chemical shifts by means of a simplified chemical language. By making use of the electronegativity concept in a quantitative manner this has turned out to be possible. Thus, in the previous example shown in figure 10, the characteristic shifts of both the NO_2 and NH_2 groups can be quantitatively correlated with their structure, and shifts can be discussed in terms of concepts like for instance inductive effect, resonance effect, group shifts or group electronegativities.

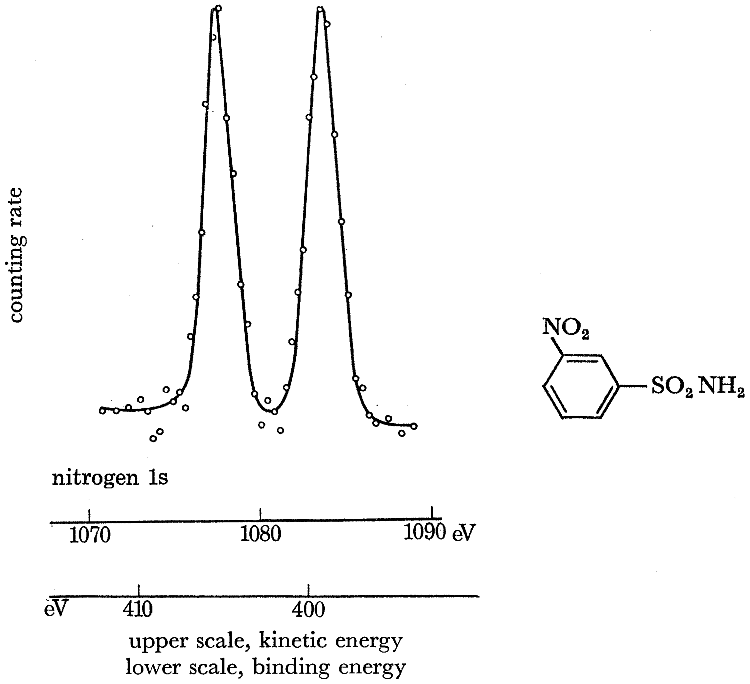


Figure 10. Nitrogen 1s electron spectrum from 3-nitrobenzenesulfonamide.

If we proceed further along the first row of the Periodic System from carbon and nitrogen we come to the equally important element oxygen. Oxygen, like carbon and nitrogen, plays a dominating role in organic chemistry. It is also of particular practical interest in connexion with surface reactions like corrosion, e.s.c.a. can be used to give information on such phenomena. As mentioned before one can trace adsorbed or chemically bound oxygen on a metal surface, either by recording the oxygen line itself or, when the oxygen is chemically bound, by recording the shifted metal oxide line. Figure 11 is an example of an e.s.c.a. spectrum of oxygen in gaseous form, namely from air. By introducing an arrangement for differential pumping, gases and vapours from volatile liquids or solid sources can now be conveniently studied by e.s.c.a. In this way gas pressures of up to $130\ \mathrm{N\ m^{-2}}$ (1 Torr) in the source chamber can be used while maintaining a sufficiently low pressure ($< 1\ \mathrm{mN\ m^{-2}}$; 10^{-5} Torr) in the spectrometer. The 1s electron lines of oxygen and nitrogen in air are seen in figure 11, recorded at a pressure of $13\ \mathrm{N\ m^{-2}}$ (0.1 Torr). Furthermore, the sensitivity is high enough to allow the $2p_{\frac{1}{2}}$, $p_{\frac{3}{2}}$ spin doublet lines from atmospheric argon to be recorded, although the abundance of this gas is only about 1 % in air. The relative amounts of the three gases can be determined from the intensities of the e.s.c.a. lines (by a calibration procedure using other gases with known elemental compositions) and fit well to the known ratio in air.

There is a particularly interesting feature of the 1s oxygen line, namely the fact that it is split in two with the intensity ratio of 2:1. Such splitting of the 1s electron line was contrary to previous experience. Oxygen chemically bound to other atoms produces single lines. Figure 12 is a recording of the 1s electron spectrum from a mixture of oxygen gas and water vapour. Again the e.s.c.a. spectrum displays a 1s electron line from molecular oxygen that is split in two components, and shifted to the right one finds the 1s line of oxygen in water without any splitting. The difference between the two main peaks is due to the chemical shift effect and amounts to 3.5 eV, whereas the splitting in molecular oxygen is 1.1 eV. This splitting can be explained in the following way. At the photoemission of an electron from the 1s shell we have to consider the interaction between an s state with a spin of $\frac{1}{2}$ and the molecular orbital state ($\pi_g 2p$) in oxygen responsible for the paramagnetic property of this gas having two spins parallel with a resulting spin of 1. The resulting total spin can either be $\frac{1}{2}$ or $\frac{3}{2}$, the weights being $2\times\frac{1}{2}+1 = 2$ and $2\times\frac{3}{2}+1 = 4$, respectively. The intensity ratio should consequently be expected to be 1:2 in accordance with the experimental result. The magnitude of this 'spin'

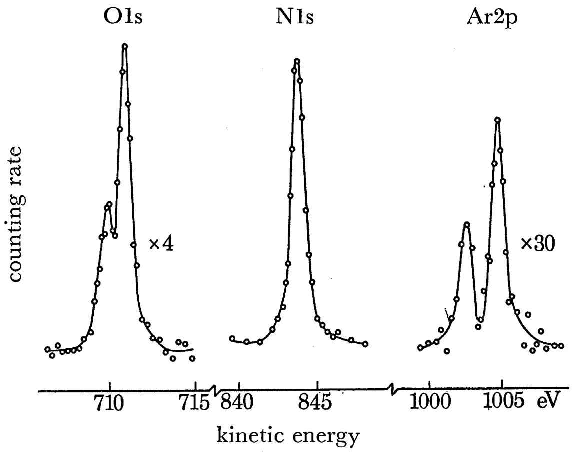


FIGURE 11. E.s.c.a. spectrum form air at 13 N m^{-2} (0.1 Torr).

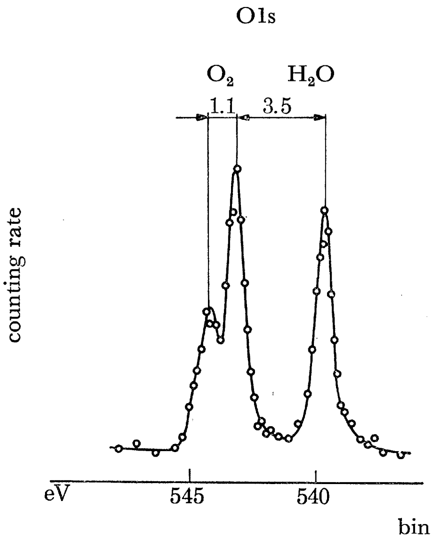


FIGURE 12. Spin splitting and chemical shift for oxygen in molecular oxygen and water, respectively.

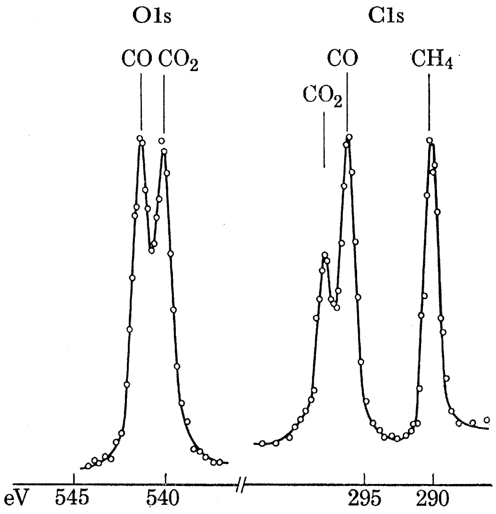


FIGURE 13. Gas analysis of a mixture of CO, CO_2 and CH_4.

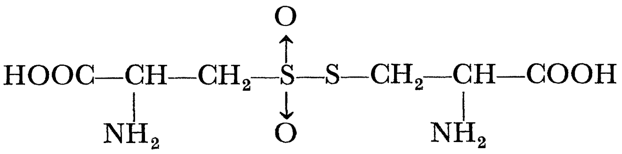
splitting can be calculated by evaluating the appropriate electrostatic exchange energy and is found to agree quite well with our value of 1.1 eV. We have verified this finding by studies also of the other two paramagnetic gases NO and NO_2.

A further example of a gas analysis at low pressure is given in figure 13. A gas mixture consisting of CO, CO_2 and CH_4 was introduced into the source chamber by needle valves at a total pressure of about 13 N m^{-2} (0.1 Torr). Because of the chemical shifts one can discriminate between the various gases, both through the O1s lines and the C1s lines. From the intensities of the lines one can conclude for example that the partial pressure of CO and CH_4 was twice that of CO_2 since the C1s lines of the three gases are in this proportion. Part of this conclusion is verified by that fact the intensities of the O1s lines of CO and CO_2 are equal. Figure 14 is another example of an analysis of a mixture of gases, namely nitrogen and ammonia. The N1s level shift between the two gases is 4.3 eV.

Chemical shifts, which reflect the character of the chemical bond which the element under inspection is subject to, can be utilized to solve chemical structure problems. A simple example is provided by the oxidation of cystine. The cystine molecule contains two equivalent sulphur atoms:

$$\mathrm{HOOC{-}CH(NH_2){-}CH_2{-}S{-}S{-}CH_2{-}CH(NH_2){-}COOH.}$$

If the cystine dioxide is synthesized two different structures may be formed. If one oxygen is attached to each of the two sulphur atoms, the resulting compound with equivalent sulphur atoms would give rise to a single line in the electron spectrum. If both oxygens are attached to one of the sulphur atoms, i.e. if the disulphide dioxide has a thiolsulphonate structure, the two sulphur atoms having non-equivalent structural positions, would give rise to two lines at different energies in the electron spectrum. According to figure 15 this is actually the case. Instead of one single line as in the symmetrical cystine, two lines are obtained from the 2p subshell in sulphur. The chemical shift is 4.0 eV. The electron spectrum of cystine *S*-dioxide therefore gives conclusive evidence for the thiolsulphonate structure:



$$\mathrm{HOOC{-}\underset{\underset{\displaystyle NH_2}{|}}{CH}{-}CH_2{-}\overset{\overset{\displaystyle O}{\uparrow}}{\underset{\underset{\displaystyle O}{\downarrow}}{S}}{-}S{-}CH_2{-}\underset{\underset{\displaystyle NH_2}{|}}{CH}{-}COOH}$$

A number of other structure problems more complicated than the above quoted example have already been solved by means of the e.s.c.a. technique. It is likely that with the improved resolution now under development still more detailed information can be obtained on structure problems for practical use.

Hydrogen bonds have turned out to play an essential role in for example biological systems. A hydrogen bridge tends to equalize the charge on the two atoms joined together by the bridge. Since e.s.c.a. is sensitive to atomic charges one may look for chemical shifts caused by hydrogen bonds. A simple case is given by acetic acid. In its monomer form this molecule contains two oxygens, one bound to carbon with a double bond, the other bound to carbon and hydrogen with single bonds. The two oxygens therefore acquire different charges in the monomer. At the vapour pressure of room temperature the acetic acid appears largely as a dimer, but at a pressure of 13 N m^{-2} (0.1 Torr) the monomer is still dominating. If the vapour is condensed on the surface of a cold trap one can expect a polymerization through hydrogen bridges between the two different oxygens according to figure 16. The charge transfer between the differently charged oxygen atoms upon solidification through the hydrogen bridges is nicely demonstrated in the e.s.c.a. spectra when the two oxygen lines merge into one.

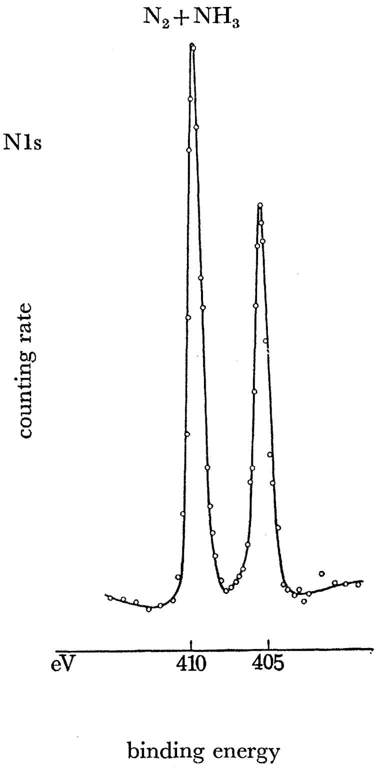


FIGURE 14

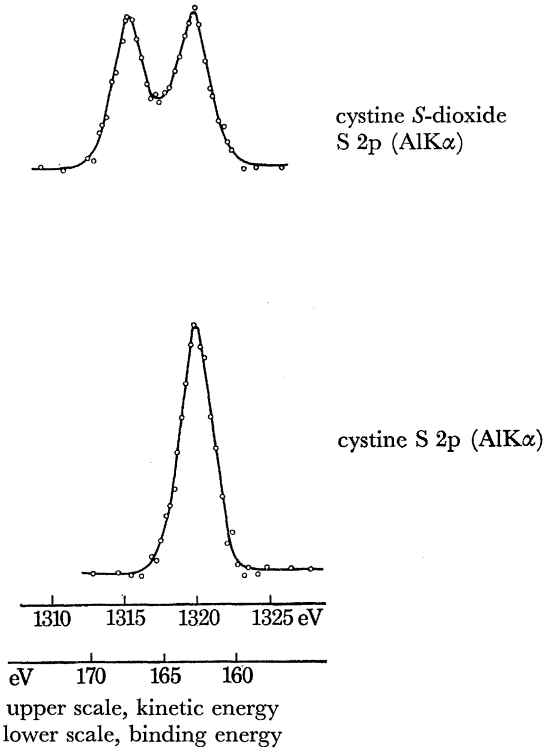


FIGURE 15

FIGURE 14. Gas analysis of a mixture of nitrogen and ammonia. The N1s shift between the two gases is 4.3 eV.

FIGURE 15. Electron spectrum from the 2p shell of sulphur in cystine *S*-dioxide and cystine. The valence states of the sulphur atoms can be determined from the spectra.

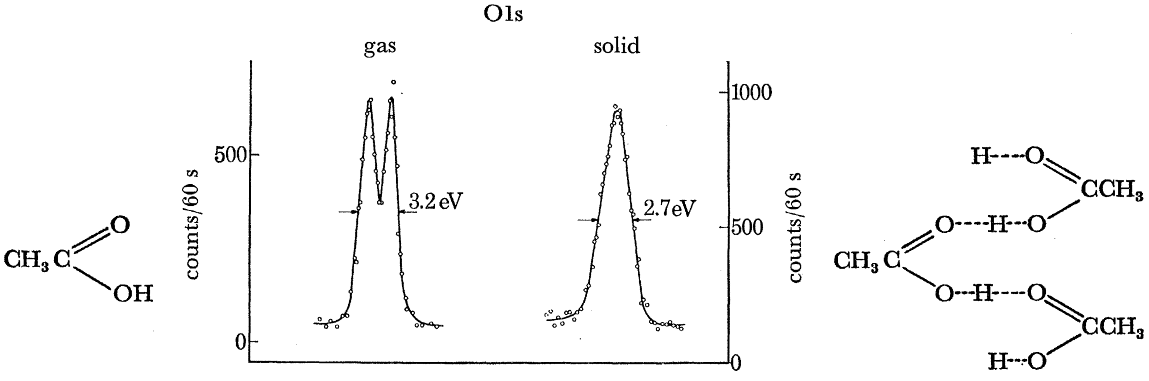


FIGURE 16. Hydrogen bond formation when 13 N m^{-2} (0.1 Torr) acetic acid is solidified by freezing as observed in e.s.c.a. The two differently charged oxygen atoms are equalized through the hydrogen bridges.

THE CHEMICAL SHIFT EFFECT

For analytical purposes the chemical shifts can be used to give additional structural information to pure elemental. From a theoretical point of view an even more intriguing possibility is to try to correlate more precisely the experimentally observed shifts to detailed and quantitative descriptions of chemical bonds. The first and simplest approach is to establish correlations between observed shifts and atomic charges in various molecules for a given element calculated according to Pauling's electronegativity rules and anticipated resonance structures. This approach has the virtue of yielding information of significance in terms of the common language of chemistry. The second step is to improve this model in various ways, for example by incorporating second-order effects like the influence of other chemical groups (inductive effects) in the molecule, i.e. consideration of a molecular potential besides the potential caused by the charge on the atom directly involved in the bond under study. The third step is to use parametrized, semi-empirical quantum mechanical calculations (like the scheme c.n.d.o.—'complete neglect of differential overlap'), which can be performed with a modest amount of computer time. Finally, the fourth step is to perform more ambitious and elaborate *ab initio* calculations, which require big computers and long machine times. The latter approaches naturally are the more realistic ones since the somewhat oversimplified but still useful *ad hoc* concepts like electronegativity, etc., do not come into play but rather the well established quantum mechanical wavefunction description as applied within the field of quantum chemistry. Our group is getting more and more involved in these various approaches as the experimental technique is being improved and more accurate information on the chemical shift effect is accumulating. We feel that e.s.c.a. is potentially able to provide the kind of experimental information which is useful for progress in this field.

In order to get an idea of how the chemical shift of a core level comes about we can imagine a diatomic molecule with atoms A and B. The atomic radius of A is r and the distance between the two nuclei is R. If we for simplicity assume an ionic bond between A and B a charge qe is transferred from the valence shell of A (at a distance r from the nucleus of A) to the valence shell of B. According to classical electrostatics the energy shift of the core electrons then becomes:

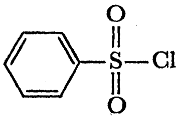
$$\Delta E = \left(\frac{1}{r}-\frac{1}{R}\right)q.$$

A better approach is to use the corresponding quantum mechanical expectation values. In an ordinary molecule the last term should more generally be replaced by an average potential of the remaining molecule. In an ionic crystal a summation over all lattice points should be performed, similar to the calculation of the Madelung constant. It is found that this simple model gives a surprisingly good estimate of the actual chemical shifts, being approximately equal for different core levels and of the order of 5 eV per degree of ionization.

Using the simple Pauling picture the partial ionic character I of a bond is obtained from the electronegativities χ_A and χ_B through

$$I = 1-\exp\left[-0.25(\chi_A-\chi_B)^2\right].$$

The charge of an atom in a molecule can then be approximately estimated by taking the sum of the partial ionic character of the bonds to the next neighbours with appropriate signs. Using this approach observed shifts for large series of compounds with widely varying structures have been correlated with the calculated charge for elements like nitrogen, carbon, sulphur, etc. Figure 17 shows the result for a number of sulphur groups based on measurements of (some 100) sulphur compounds with sulphur in various oxidation states and chemical environments. With this simple method surprisingly good correlations are obtained. To give an idea of the procedure we shall explain how the charge is calculated for an organic sulphur group and we shall take the aromatic sulphonyl group as an example:



benzenesulphonylchloride

In this molecule there is one S—C bond, four S—O bonds, and one S—Cl bond. The electronegativities of sulphur and carbon are equal, 2.5, and this bond gives no contribution to the charge on sulphur. The electronegativity difference between sulphur and oxygen is

$$|2.5-3.5| = 1.0.$$

This corresponds to $I = 0.22$, and there is a contribution to the charge on sulphur of

$$+4\times 0.22 = +0.88.$$

Similarly, for the S—Cl bond the electronegativity difference $|2.5\text{–}3.0| = 0.5$ gives a contribution of $+0.07$. The charge on the sulphur is thus estimated to be $0+0.88+0.07 = +0.95$.

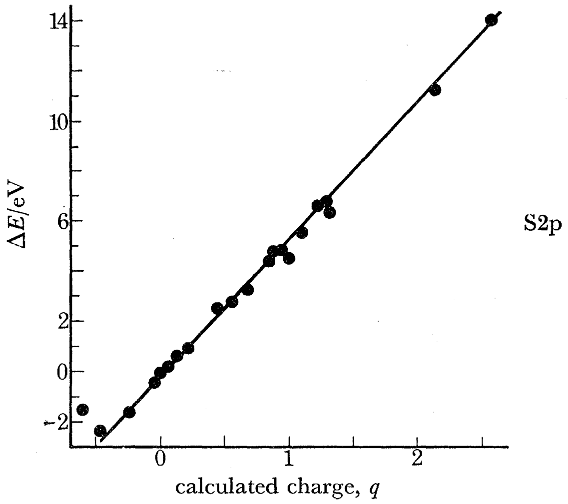


FIGURE 17. Correlation of sulphur binding energies with Pauling charge in various groups of sulphur compounds.

With substituents in the aromatic ring exerting strong inductive and mesomeric effects, it has by a systematic study of substituted series been possible also to observe substituent effects on the binding energies of sulphur in aromatic sulphur groups, although they are rather small compared to the first-order effects from the nearest neighbours. The fact that the greatest influence on the shifts normally is exerted by the nearest neighbours, makes it possible to derive characteristic group shifts, which can be used in structure studies. Using the shift–charge correlation the group shifts can also be expressed in terms of group electronegativities, which are particularly useful for carbon compounds. Calculating the charge by means of an iteration procedure using the experimentally obtained group electronegativities gives an improved correlation, which now also takes account of inductive effects from atoms situated further away in the molecule than the next neighbours.

Finally this simple method can be used for a rough estimation of the relative contributions of different resonance structures, if the same type of calculation as exemplified above is applied to the different canonical structures. The experimental shift then gives their relative weight in the assumed resonance hybrid.

THE POTENTIAL MODEL

We have also performed *ab initio* m.o.-s.c.f. calculations on a series of molecules containing carbon and sulphur in order to obtain, in a more well-founded way, realistic charges on the nuclei involved. The calculations were performed by means of the computer program IBMOL version 4, developed by Clementi, Davies and Veillard. Large basis sets of gaussian type functions including also polarization functions were used in these calculations. The charges were obtained by a population analysis of the final wavefunctions. The Mulliken definition of gross atomic charge was chosen.

Figure 18 shows the correlation between experimental chemical shift in the S2p level and calculated gross atomic charge on sulphur for a series of free molecules containing sulphur. The correlation is well described by a straight line with the slope 4.7 eV per unit charge. However, from a theoretical point of view it is not obvious that the chemical shift should be directly correlated to the charge on the considered atom. In order to more fully understand this let us again discuss the nature of the chemical shift, this time in a somewhat more strict and general way.

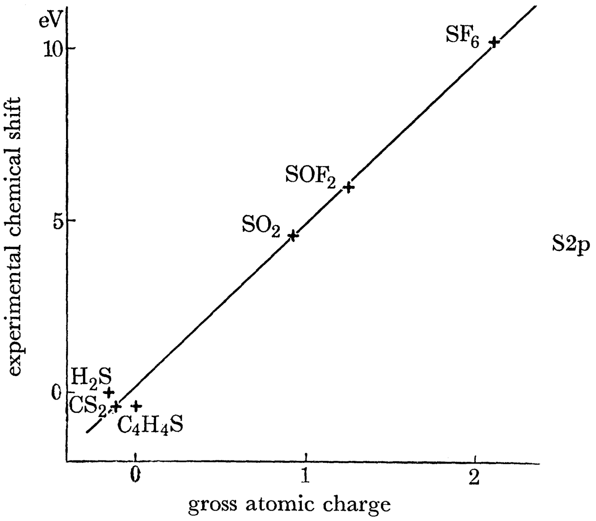


FIGURE 18. Experimental chemical shifts for sulphur 2p electrons plotted against gross atomic charge on sulphur.

In a complete description of electron binding energies and their chemical shifts consideration must be taken also to the effect of the reorganization occurring among the remaining electron orbitals upon ionization of a core level. However, when discussing chemical shifts this effect can usually be disregarded since the difference in reorganization energy is believed to be rather small for an inner shell. Therefore the chemical shifts can be discussed in terms of shifts in orbital energy.

A core electron in a molecule can be considered to be completely localized to its mother atom. Its orbital energy will hence be fully determined by the electrostatic potential close to this nucleus. This potential, of course, is set up by the charge distribution within the whole molecule. Chemical shifts consequently are due to changes in this local potential set up by differences in charge distributions for different molecules. However, the exact meaning of charge distribution and potential, being functions over the three-dimensional space, is too complicated to be easily treated in a more general model for the chemical shift. This difficulty can be overcome by condensing the charge around each nucleus in the molecule to point charges at the nuclei positions. The change of the local potential determining the chemical shift can be considered as obtained from a superposition of two potentials. The first, which generally is the dominating, originates from the change in electronic distribution around the particular nucleus being studied within the molecule. The second potential, which we may call the molecular potential, is set up by the charge distribution from the rest of the molecule. The molecular potential is easily estimated having condensed the charges to point charges. The first potential obviously is not well described by a point charge at the position of the nucleus. However, from comparisons with free atoms and ions it can be expected to be approximately proportional to the charge on the atom. The chemical shift ΔE_i of a specific inner level in atom i in a molecule can now be approximated by

$$\Delta E_i = kq_i + V_i + l, \tag{1}$$

where

$$V_i = \sum_{j \neq i} \frac{q_j}{R_{ij}} \tag{2}$$

and q_i, the charge on atom i; k, the proportionality constant specific for the inner level studied; V_i, the molecular potential at atom i; R_{ij}, the distance between nuclei i and j; l, a constant determined by the choice of reference level. The magnitude of the constant k can be obtained from calculations on free atoms and ions. For 1s electrons in carbon it is about 18 eV per unit charge and for 2p electrons in sulphur it is about 14 eV per unit charge. Equation (1) is also approximately valid for ionic crystals. The potential V_i is then a crystal potential which can be obtained by using the Madelung constant.

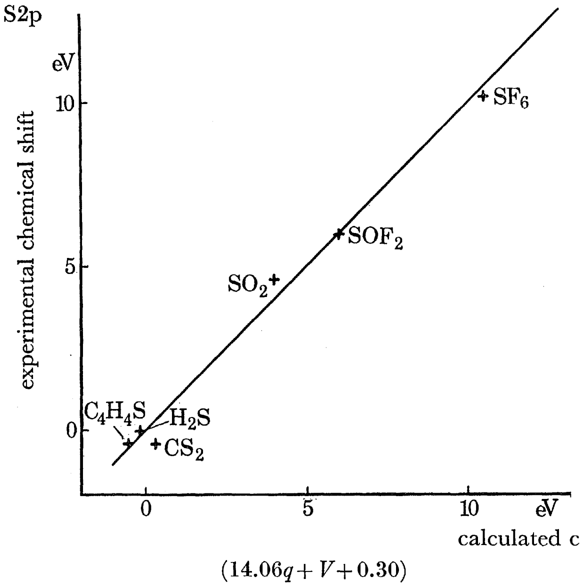


FIGURE 19. Experimental chemical shifts for sulphur 2p electrons plotted against chemical shifts calculated from the potential model.

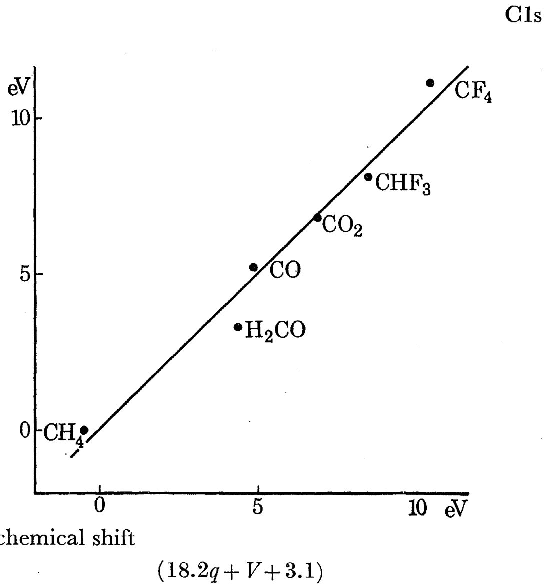


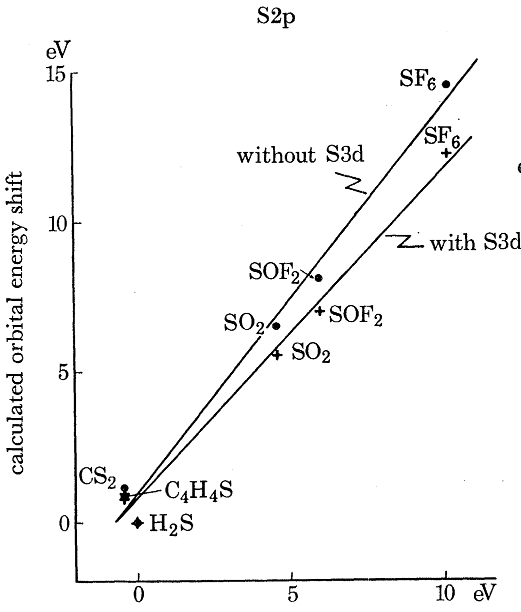
FIGURE 20. Experimental chemical shifts for carbon 1s electrons plotted against chemical shifts calculated from the potential model.

In order to test the simple potential model (1) energy shifts were calculated by using the gross atomic charges obtained from the *ab initio* m.o.-s.c.f. calculations mentioned above. Figures 19 and 20 show the correlations obtained between calculated chemical shifts and experimental chemical shifts of sulphur and carbon in some molecules. The proportionality constant k for each correlation was optimized to give a least squares fit. The result was 14.1 eV per unit charge for the sulphur correlation and 18.2 eV per unit charge for the carbon correlation. In both cases the agreement with the values expected from calculations on free atoms and ions is very good which indicates that the approximations in the potential model seem to be fairly justified and that the magnitudes of the calculated gross atomic charges are realistic.

Let us now return to the former correlations where the chemical shift was correlated directly to the charge on the considered atom. From relation (1) follows that if the molecular potentials V_i are directly proportional to the gross atomic charges q_i then the chemical shifts ΔE_i fulfil the linear relation

$$\Delta E_i = Cq_i + l,$$

where C is a constant. From the results of the *ab initio* calculations we verified that for the molecules studied such an approximate linear relation between molecular potential and gross atomic charge really exists. For diatomic molecules and molecules where the studied atom enters as central atom, the explanation is given by the approximately constant bond length for the considered atom. For large molecules it is not obvious that such a linear relation should hold. However, the correlations of e.s.c.a. shifts with charge indicate that even in these cases the approximate linear relation is valid.



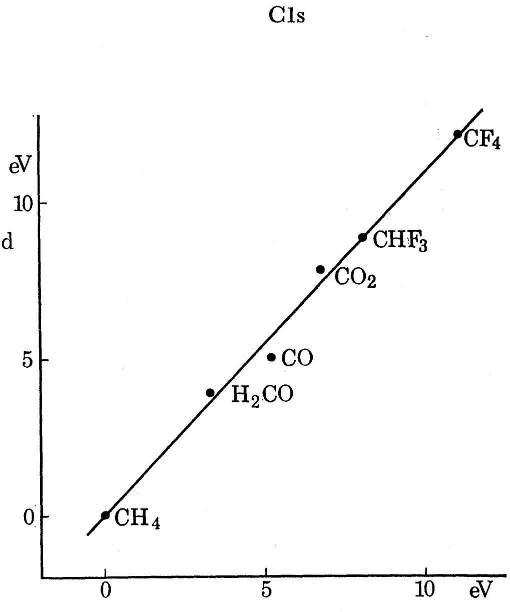


FIGURE 21. Calculated shifts in sulphur 2p electron orbital energy, with and without sulphur 3d polarization functions, against experimental chemical shifts.

FIGURE 22. Calculated shifts in carbon 1s electron orbital energy against experimental chemical shifts.

Ab initio calculations on molecules give in contrast to most semi-empirical calculations solutions also for the inner electrons. It is then possible to make direct comparisons between experimental chemical shifts and calculated orbital energy shifts. Figures 21 and 22 show the correlations obtained for sulphur 2p and for carbon 1s chemical shifts, respectively. In figure 21 is given both the correlation with and without sulphur 3d polarization functions in the basis set. The effect of these latter functions is to decrease the slope of the straight correlation line from 1.29 to 1.09. Agreement between theory and experiment corresponds to the slope 1.00.

Molecular orbitals

The study of the atomic core electron lines and their chemical shifts in molecules forms the basis for e.s.c.a. as an analytical tool and as a new means for mapping out the charge distribution. As mentioned earlier in this survey the scope is, however, not limited to core electrons. Valence bond structure in solids and free molecules is of considerable current interest. The loosest bound electrons with binding/or ionization energies close to zero, say 0 to 50 eV, usually can be regarded as belonging to the entire molecule or solid and are less characteristic of any specified atomic constituent. These molecular orbitals can also be investigated in e.s.c.a. excitation by means of X-rays complement u.v. excitation in this low binding energy region to the extent that also deeper levels can be excited by X-radiation. On the other hand, due to the much smaller inherent line widths of, for example, the 21 eV helium resonance line used for u.v. excitation, the attainable resolution is higher for u.v. excitation. A particularly useful feature of X-ray excitation of molecular orbitals is the strong photo cross-section dependence for X-ray photons on the symmetry of the orbitals. By measuring these relative cross-sections for some simple atomic systems in which the orbital symmetries are known one obtains a gauge for the measurement of symmetries in the more complicated molecular orbital spectra. We have studied a series of such spectra from free molecules by e.s.c.a. and have found it possible to make fairly complete experimental assignments of both the energies and the symmetries of the molecular orbitals. New c.n.d.o. calculations on these molecules were of considerable help in the analysis. Detailed discussions are given in our recent book on *ESCA applied to free molecules* and only one spectrum with brief comments will be given here, namely CF_4.

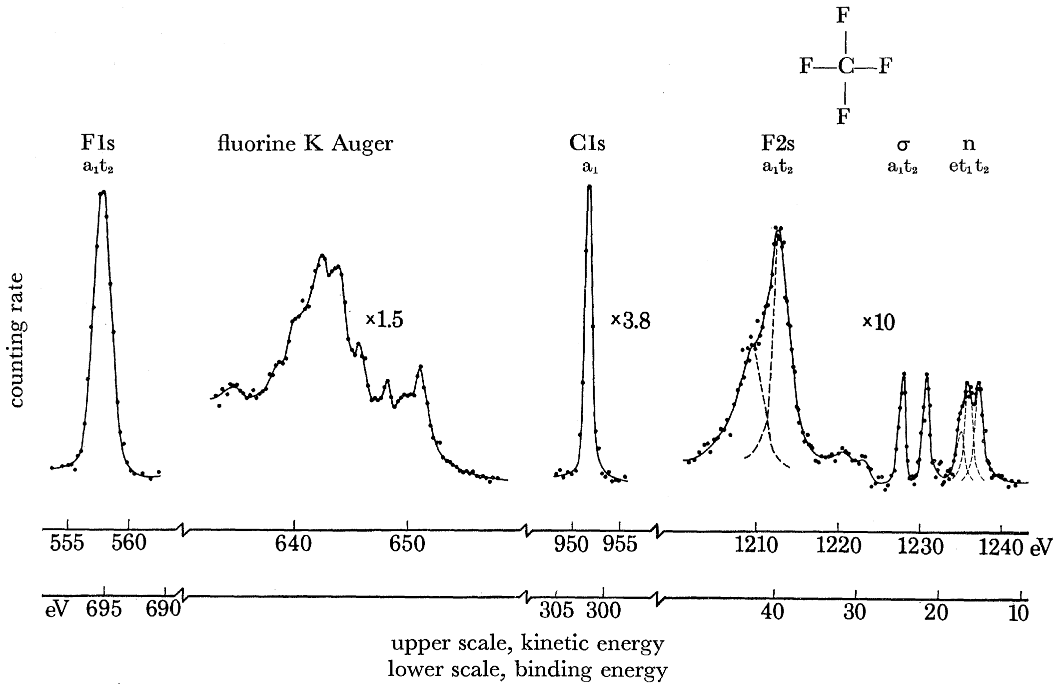


Figure 23. E.s.c.a. spectrum from carbon tetrafluoride excited by MgKα-radiation. The atomic-like core orbitals F1s and C1s, and the valence molecular orbitals are seen in this e.s.c.a. spectrum as well as the fluorine K Auger electrons.

Figure 23 shows the e.s.c.a. spectrum of CF_4, consisting of the 1s level of F, part of the fluorine

K Auger electron spectrum (in complete form some thirteen resolved lines), the 1s level of C and finally the molecular orbital spectrum from 50 to 0 eV. There is also a carbon K Auger electron spectrum between 230 and 260 eV, consisting of some 12 resolved lines which is not shown in the figure. One interesting feature of the core electron lines is that the width of F1s is appreciably larger than the C1s, far outside atomic widths systematics in this region. The valence molecular orbitals derive mainly from the atomic 2s and 2p orbitals of carbon and fluorine. There are 32 valence electrons distributed among 16 molecular orbitals but due to the high symmetry of the molecule several of these orbitals are degenerate and only seven different ionization energies are observable in the valence electron spectrum. Three of these states have previously been studed in u.v. excited spectra and are attributed to mainly non-bonding molecular orbitals. For an understanding of the chemical bonding it is of interest to study also the bonding orbitals. In figure 23 these deeper orbital states can now be seen. The deepest lying valence orbitals are $1a_1$ and $1t_2$ which are mainly of F2s character. There is a small bonding C2s contribution to the $1a_2$ orbital and a similar C2p contribution to the triply degenerate $1t_2$ orbitals. The large width of the deepest valence orbitals can be explained by an increased inherent width due to radiationless transitions of Coster-Kronig type and, to a lesser extent, to vibrational structure of these strongly bonding orbitals. The $2t_2$ has mainly C2p–F2pσ bonding character while $2a_1$ has C2s–F$(2S+2p_\sigma)\sigma$ bonding character. The non-bonding orbitals 1e, 1t, and $3t_2$ are seen to the right in the spectrum.

Molecular Auger and autoionization electron spectra

Photons of discrete energies excite electron line spectra. Electrons, on the other hand, interact with atoms through a virtual photon field with a continuous frequency distribution, and the primary electron emission at ionization is therefore characterized by a continuous distribution of electrons. With the vacancy left behind in the atom, however, various kinds of discrete energy jumps occur, either through the emission of an electromagnetic line spectrum or through the emission of an Auger electron line spectrum. We are interested in the latter alternative. There is a closely related process to consider here, too, namely the emission of autoionization electrons. In the former case the intermediate state can be thought of as a singly ionized atom, the final state being a doubly ionized one. In the latter case the intermediate state can be regarded as an excited neutral atom, the final state being a singly ionized one (either in the ground state or in an excited state of the ion). Although these descriptions are semiclassical and have to be replaced by the usual quantum mechanical description in order to give an adequate account of the dynamics they are useful from the point of view of systematics.

Molecular Auger and autoionization electron spectra have been little studied so far. Evidently, the electron source for excitation need not be monokinetic (as is the case for studies of discrete energy loss spectra of electrons). In the experiments which we have performed, the electron source has been a beam from an electron gun with an energy of a few kiloelectronvolts traversing the gas target chamber perpendicular to the emission angle of the electrons to be studied. In this way we have recorded at high resolution Auger electron spectra from all the rare gases. These spectra are very line rich and can in part be compared to transitions in u.v. spectra. An interesting field from a chemical point of view is the study of such spectra emitted from molecules. We have been able to observe chemical shifts in such spectra both for solids and gases, although in general these spectra are much more complex and more difficult to interpret than the photoelectron spectra. We have also found evidence for a vibrational structure in Auger electron lines and also in autoionization electron lines. An example of this is the carbon Auger electron spectrum of carbon monoxide (figure 24). The left part of the spectrum is the Auger part showing a closely spaced vibrational structure at the right side of a strongly excited single Auger line. Further out to the higher energy side of the spectrum there are a few autoionization electron groups with clearly resolved vibrational components.

As an example of an autoionization electron spectrum of a rare gas figure 25 shows a high resolution study of argon. Particular features of these spectra, in full accordance with the more detailed theoretical description of the process, are the characteristic emission- or absorption-like

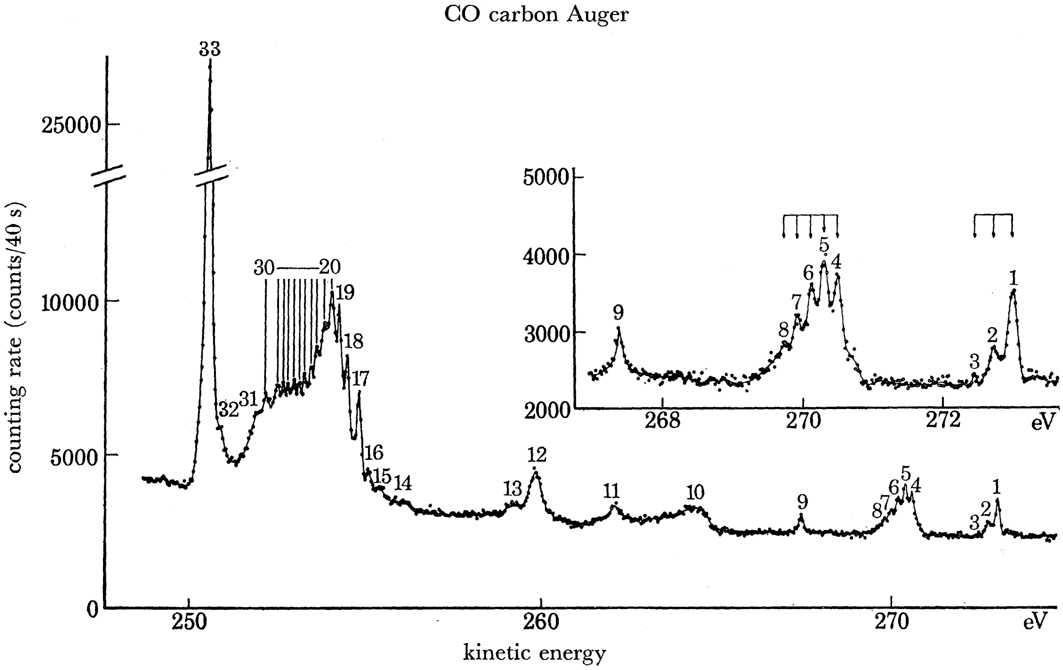


FIGURE 24. Part of the carbon Auger and autoionization electron spectrum from CO excited by electron impact. The insert figure shows the vibrational structure in some of the autoionization lines.

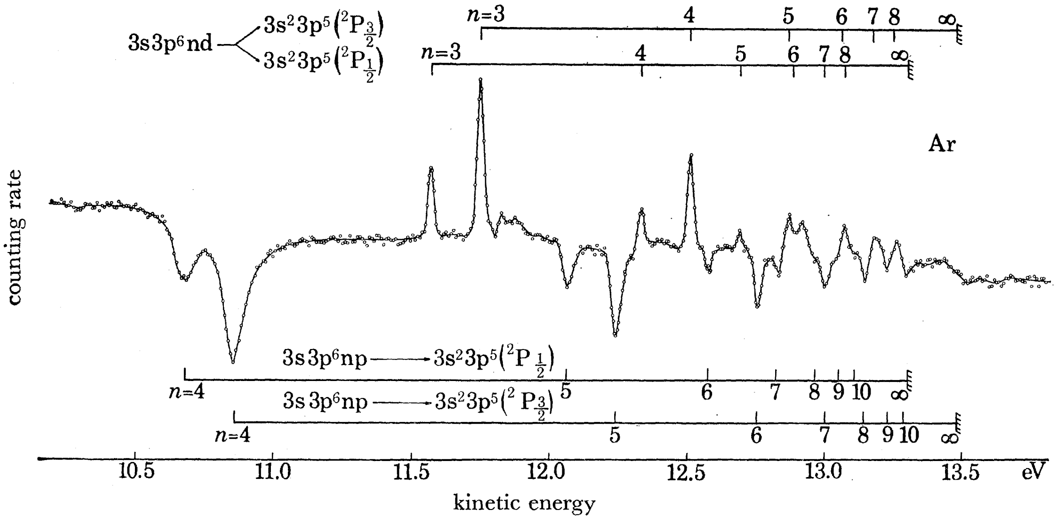


FIGURE 25. Autoionization electron spectrum from argon showing four identified series of lines.

line profiles. Several Rydberg series can be identified in this spectrum with series limits corresponding to a second ionization. The appearance of the two upper Rydberg series in the figure can be assigned to the spin-orbit splitting of the 3p shell (being an order of magnitude smaller than the 2p spin-orbit splitting as observed in the Auger electron spectrum). The splitting of the two line series is 0.18 eV and the intensity ratio between them is 2:1. It is interesting to note that these findings are in close agreement with what we previously have observed by means of photoionization of argon using the He resonance radiation at 21 eV for excitation. This doublet is shown in figure 26*a*. The resolution in this experiment, defined as the full width at half maximum height of the electron line, is 13 meV.

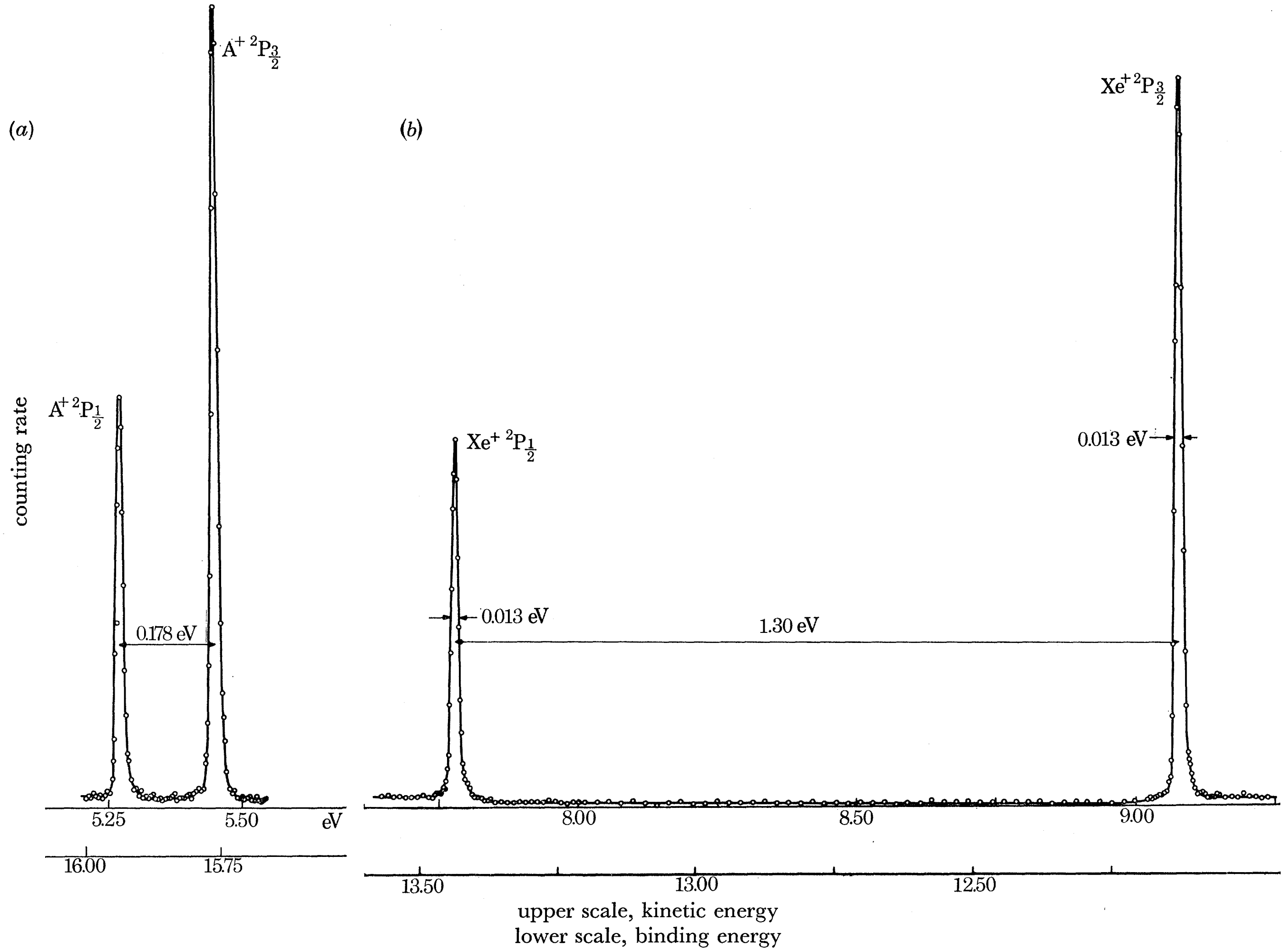


FIGURE 26. Electron spectrum of (*a*) argon and (*b*) xenon showing the spin-orbit splitting of the $3p^5(^2P)$ term and $5p^5(^2P)$ term, respectively. The spectra were excited by helium resonance radiation at 21.21 eV.

MOLECULAR VIBRATION AND ROTATION

The resolution in u.v. excited electron spectra for small molecules in the gaseous phase is ultimately set by Doppler broadening due to the thermal motion of the molecule and, in case the vibrational structure can be resolved, to the rotational envelope of each vibrational line. This is illustrated in figure 27*a* and *b* showing the vibrational structure of hydrogen ($H_2^+ X\ ^2\Sigma_g^+$).

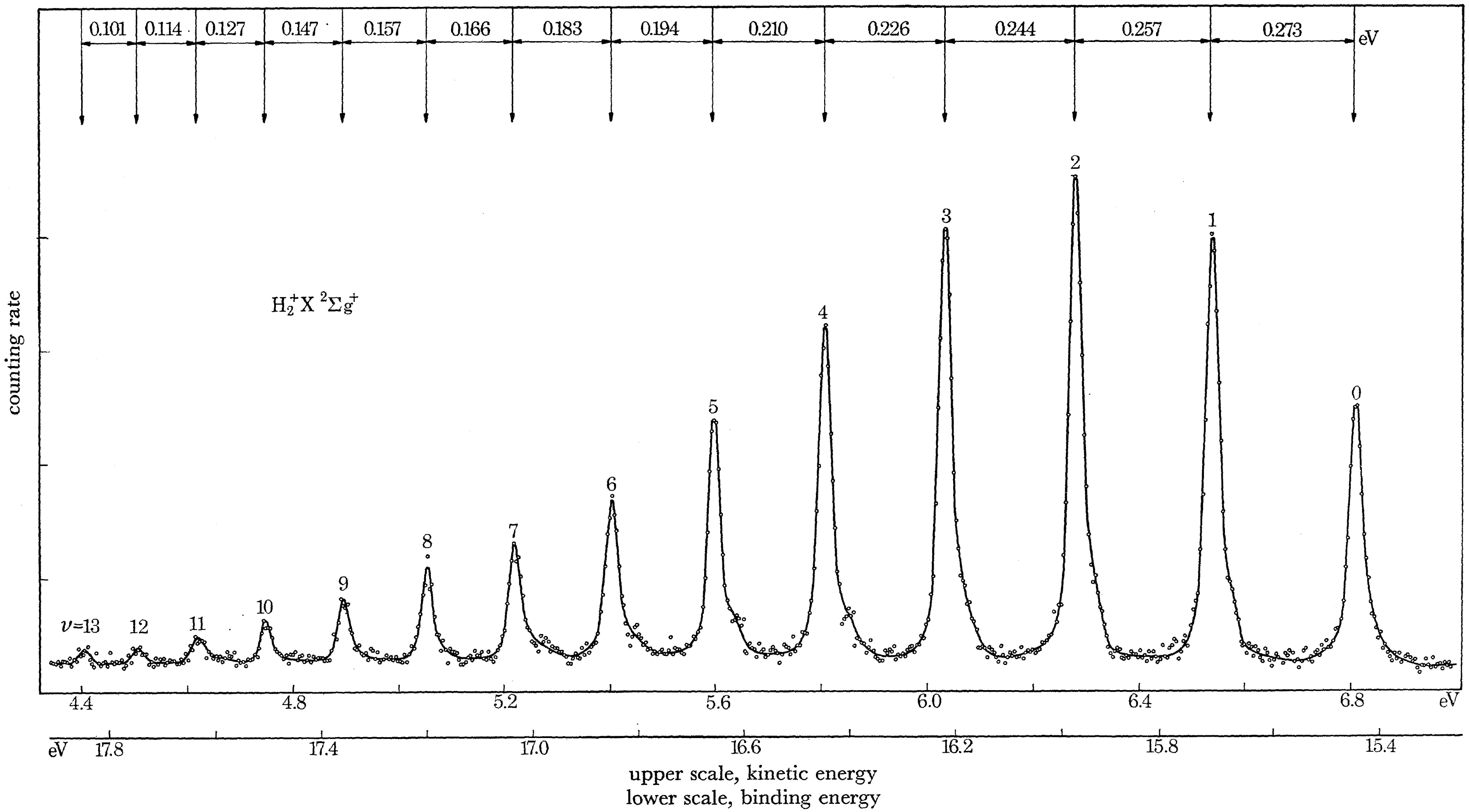


FIGURE 27*a*. Electron spectrum from molecular hydrogen, excited by helium resonance radiation. Fourteen peaks are seen which correspond to vibrational levels of the molecule ion.

Fourteen peaks are observed in this spectrum and the distances between them correspond well with the calculated ones. The intensities are determined by the Franck–Condon factors for the transitions. The line widths are in this case broader than in the previous case of argon because of the following reasons: 1, the Doppler width for this much lighter molecule is larger, around 20 meV; 2, the rotational structure (absent in argon) is presently impossible to resolve within each vibrational line and consequently adds to the linewidth. It is tempting to try to improve the techniques somewhat in order to be able to resolve rotational structure. Looking at figure 27 *b* one can already observe some indication of this rotational structure (the expected rotational lines are indicated by arrows). The spectrometer resolution ($\Delta E/E \approx 5 \times 10^{-4}$) is already adequate for this. If the Doppler broadening were removed by cooling the gas and/or by directing the gas flow perpendicular to the electrons to be studied and, furthermore, if every second rotational line were removed by using para hydrogen, resolved rotational structures in hydrogen could probably be recorded.

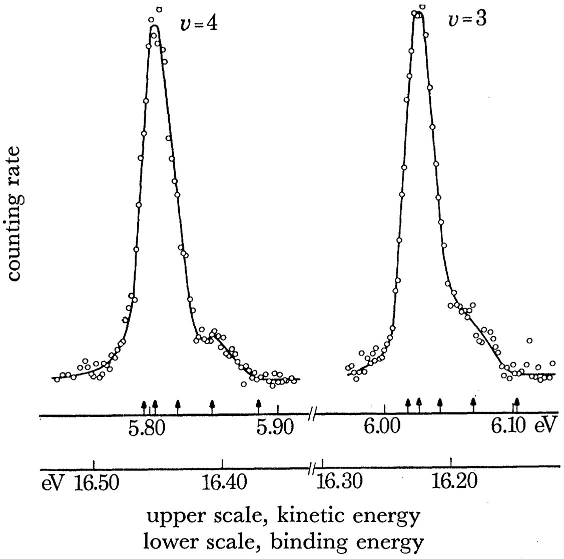


FIGURE 27 *b*. More detailed recordings of the peaks corresponding to $v = 3$ and $v = 4$ for the molecule ion, showing rotational structure. The arrows indicate the positions of some of the individual rotational peaks for which $\Delta J = 0$.

PHOTOIONIZATION DYNAMICS

Another important feature apart from high resolving power, which should be taken into consideration is the signal-to-background ratio. Improvements in this respect open up the possibilities to observe also weak but theoretically significant features in the electron emission dynamics. As an example of such processes figure 28 shows the electron spectrum of Ne excited by MgKα X-radiation. The 1s electron line spectrum of Ne is recorded with an emphasis to study the 'shake up' spectrum of Ne. On both sides of the main line a number of satellite lines are observed. The intensities of these lines are less than 10 % of the main line which has been reduced in intensity by a factor of 20 in the figure. The satellite lines have three different origins. The high energy lines are due to the high energy satellite lines in the incoming X-radiation. Photoelectrons from the neon 1s shell induced by the more energetic X-ray satellites in Mg(Kα', α^3, α^4, α^5, α^6 and the diagram line Kβ) will consequently have higher energy. The Kα_3 and α_4 satellites are due to KL double hole states and the Kα_5 and α_6 satellites to KLL triple hole states of the emitting magnesium atoms. The Kβ band of magnesium involves the transition of a valence bond electron to the K shell. The low energy part of the spectrum contains a number of lines superimposed on a broad continuum starting sharply around 362 eV and extending some 50 eV toward lower electron kinetic energies. The intensity of the continuum and the structure 1–4 in the figure measured relative to the main line is found to be pressure dependent. They are therefore interpreted as due to secondary collisions between ejected photoelectrons and neutral atoms. There is a close correspondence to the optical spectrum of NeI and the energy loss spectrum. For example, line 2 with the energy loss 16.8 eV is thus identified as the 2p → 3s transition excitation by Ne1s photoelectrons and line 3 at 20.0 eV fits the 2p → 3d transition.

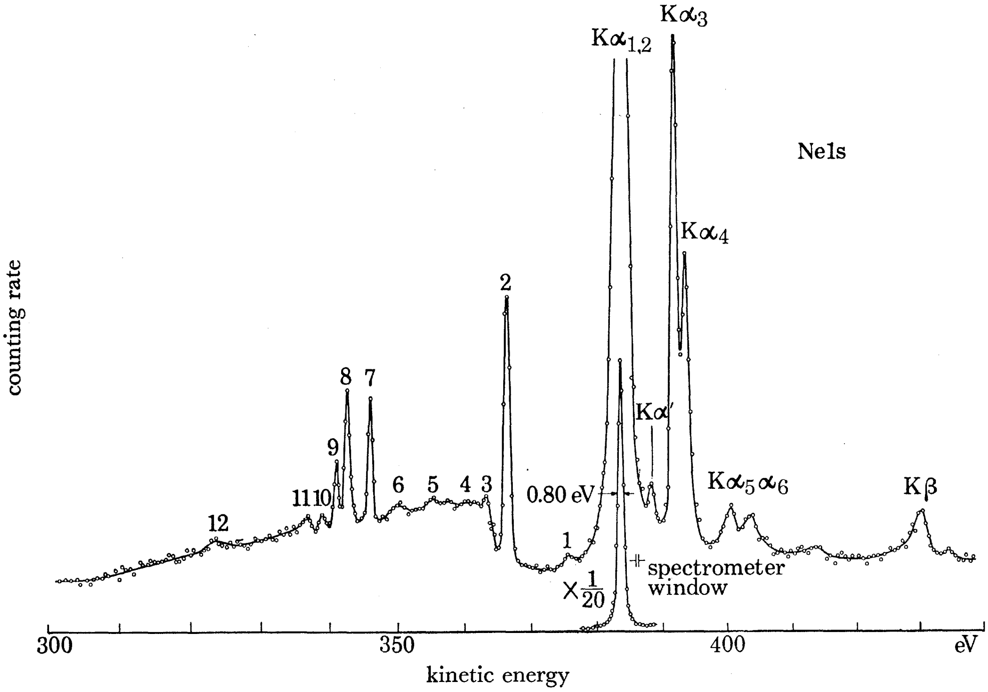


FIGURE 28. Neon 1s electron spectrum excited by MgK radiation. The main peak is the Ne1s line excited by MgK$\alpha_{1,2}$. The MgK X-ray satellites and Kβ radiation give the peaks with higher kinetic energy. The peaks with the lower energies (number 1–12) are due to shake up, shake off and inelastic scattering.

The remaining lines, 5–12 in the spectrum, are independent of pressure and are due to ionization processes at which a valence electron is simultaneously ejected or excited. The former is called shake off and the latter we call shake up.

A theoretical study of the possible shake up states indicates that only states of the types $1s\,2s^2 2p^5 np\,^2S$ and $1s\,2s\,2p^6 ns\,^2S$ have to be considered and that the excitations are due to monopole transitions. Calculations were performed on a number of neon states with the help a numeric Hartree–Fock program. It turns out that lines 7–11 are due to shake up processes of the first type and line 12 of the second type. The complete shake off of a 2p electron, i.e. the ionization limit of the first-term series, occurs close to line 11 at an excitation energy of 47 eV. The shake-up states have three unpaired electrons. Using a multiconfigurational s.c.f. procedure the term splitting could be calculated for $n = 3$, 4 and 5. Thus, lines 7 and 8 could be identified as a lower and upper doublet state, respectively, in the term $Ne^+\,1s\,2s^2 2p^5 3p$, lines 9 and 11 as a lower and upper state in $Ne^+\,1s\,2s^2 2p^5 4p$ and line 10 as the lower state in

$Ne^+ 1s 2s^2 2p^5 5p$. Compared to the experimental spectrum the calculated energies relative to the main Ne1s line are consistently displaced toward lower energies by about 1.8 eV. The spacing between the states is very close to that experimentally observed, however. These findings may be explained in the following way: The main line represents a state with one 2p electron pair more than the shake up states. There will thus be a larger electron correlation energy for the main 1s hole state than for the shake up states. If the s.c.f. calculations, which omit the correlation energy, are accurate enough, the difference found between the observed state energies and the calculated ones should yield an approximate value of the electron correlation energy for a 2p electron in $Ne^+ 1s 2s^2 2p^6$ since the relativistic correction is an order of magnitude smaller, i.e. $E_{corr} \approx 1.8$ eV, which is a reasonable numerical value.

Final remarks

The field of electron spectroscopy is now in a stage of rapid development.

As a tool, electron spectroscopy is an alternative and a complement to other established spectroscopies. For example, new information on molecular charge distribution, chemical bonds, and molecular orbitals has now become available. These data can be correlated to chemical model concepts and to quantum mechanical calculations of various degrees of sophistication. Other applications are indicated by some examples in this survey. It is reasonable to assume that the scope is wide enough for several further developments.

It is a pleasure for me to acknowledge the cooperation of my colleagues at Uppsala in the research work described in this survey. No literature references have been given here; instead the reader is referred below to our two books, which contain extensive publication lists.

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