

X-Ray Emission Spectroscopy

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1 Introduction

X-Rays were discovered by Roentgen¹ in 1895. This form of electromagnetic radiation is emitted whenever matter is irradiated with high energy electrons, as in the Crooke's tube of Roentgen's original experiment. It was found that each element could be induced to emit X-rays of particular wavelengths characteristic of that element. Moseley² demonstrated a direct relationship between atomic number and the square root of the reciprocal of the wavelength of the $K\alpha$ X-radiation of an element. The mechanism for the formation of X-rays is simple.³ A vacancy is created in an inner orbital of an atom; this vacancy is then filled by an electron from an outer orbital and the energy of the quantum of X-radiation emitted corresponds to the difference in ionisation energies between the two orbitals. Since atomic orbital ionisation energies are characteristic of an atom, so also are the wavelengths of the X-radiations which the atom emits. Clearly, the number of possible X-transitions will be greater in larger atoms so that the complexity of an X-ray emission spectrum increases with atomic number. No inner vacancies can be created in hydrogen and helium and only one X-ray transition is possible for the first row elements lithium—neon.

The X-rays of common experience have wavelengths in the range 0.01—0.5 nm, *i.e.* approx. 125—2.5 keV, but there really is no distinction between this region, the soft X-ray region 0.5—20 nm, and the vacuum u.v. region 20—200 nm, save that imposed by instrumentation. The relationship between energy and wavelength is $E = \frac{1239.8}{\lambda(\text{nm})} \text{ eV}$

Not only electron bombardment of atoms causes X-rays to be emitted. X-Radiation itself can cause photo-ionisation of inner electrons and a characteristic X-ray will be emitted as the vacancy is filled. In both electron and X-ray irradiation it is, of course, necessary that the energy of the incident particle or photon should be greater than the ionisation energy of the electron, otherwise the vacancy in that orbital would not be generated and so X-rays characteristic of the transition to that orbital would not be observed.

The various possible X-rays that can be emitted by an atom are classified according to the orbital in which the primary vacancy was created. The nomenclature is archaic, cryptic, and widely used. Transitions to a vacancy in the K

¹ W. C. Roentgen, *Ann. Physik u. Chem.*, 1898, **64**, 1.

² H. G. J. Moseley, *Phil. Mag.*, 1913, **26**, 1024.

³ A. H. Compton and S. K. Allinson, 'X-Rays in Theory and Experiment', Van Nostrand, New York, 1935.

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shell, principal quantum number 1, give rise to *K* spectra, the particular transition being distinguished by a combination of greek letters and arabic numbers. Transitions usually take place between closed shells and shells with a single vacancy, spin orbital coupling therefore gives two values of *j* for each value of *l* (unless *l* = 0). Thus, a transition from a *2p* shell to a *1s* vacancy in a light element gives rise to a $K\alpha_{1,2}$ X-ray. The 1 and 2 refer to the two possible $2p^5$ states, $^2P_{3/2}$ and $^2P_{1/2}$, which in a light element would have very similar energies; in a heavy element $K\alpha_1$ and $K\alpha_2$ would be observed as separate emission lines. Transitions to a vacancy in the second shell give rise to *L* spectra, to a third shell vacancy give *M* spectra, etc. Possible transitions, with their symbols, are shown in Figure 1.

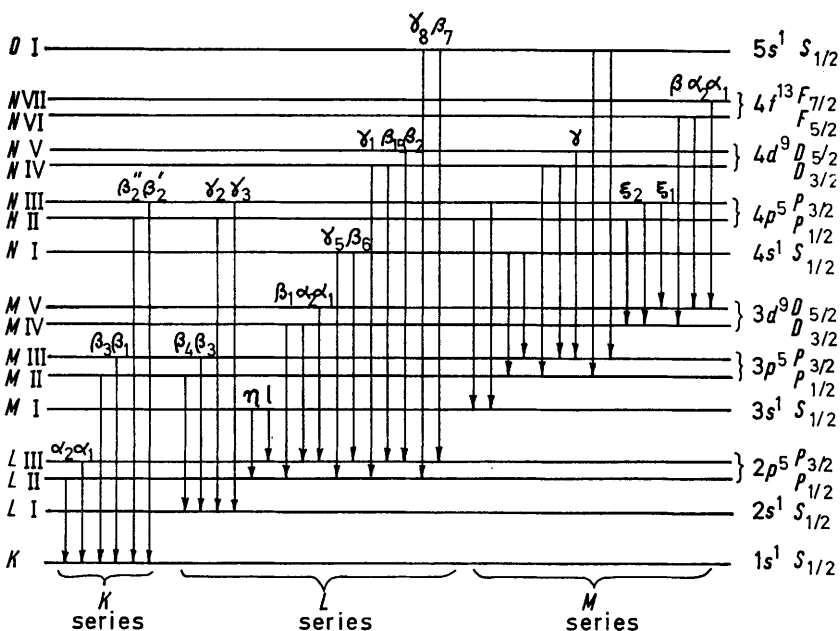


Figure 1 Permitted X-ray emission transitions. Electron configurations, and the corresponding spectroscopic state are indicated on the right

The observed emissions are those permitted by the atomic selection rules $\Delta l = \pm 1$, $\Delta j = \pm 1, 0$, which is why $2s \rightarrow 1s$ etc. transitions are absent from Figure 1. The actual intensities of the 'permitted' emissions vary widely. A variety of factors is involved. If all other things are equal then the number of electrons is the deciding factor. Four electrons contribute to the $^2P_{3/2}$ state but only two to the $^2P_{1/2}$ state, thus the $K\alpha_1: K\alpha_2$ intensity ratio is about 2:1. When transitions to a common vacancy from a variety of orbitals are being considered a primary factor is the physical overlap in space of the two orbitals

concerned in the transition. Thus, a transition to a $1s$ vacancy from a $2p$ orbital, $K\alpha$, will be more intense than a transition from a $3p$ orbital, $K\beta$. This can sometimes result in certain emissions being very weak indeed due to the following mechanism. If $2s$ and $2p$ orbitals overlap considerably then a vacancy in the $2s$ orbital will almost always be filled by an electron from a $2p$ orbital, and all other possible L_1 spectra will be very weak.

Other possible causes of intensity variations involve the passage of the photon from the atom. As the atomic number decreases so the probability that this photon will be internally converted increases tremendously. This means that the photon never leaves the atom but its energy is used to eject an outer electron with a kinetic energy equal to the energy of the photon less the binding energy of the electron. The detection of such Auger electrons⁴ can prove just as important in element identification as the observation of characteristic X-rays.

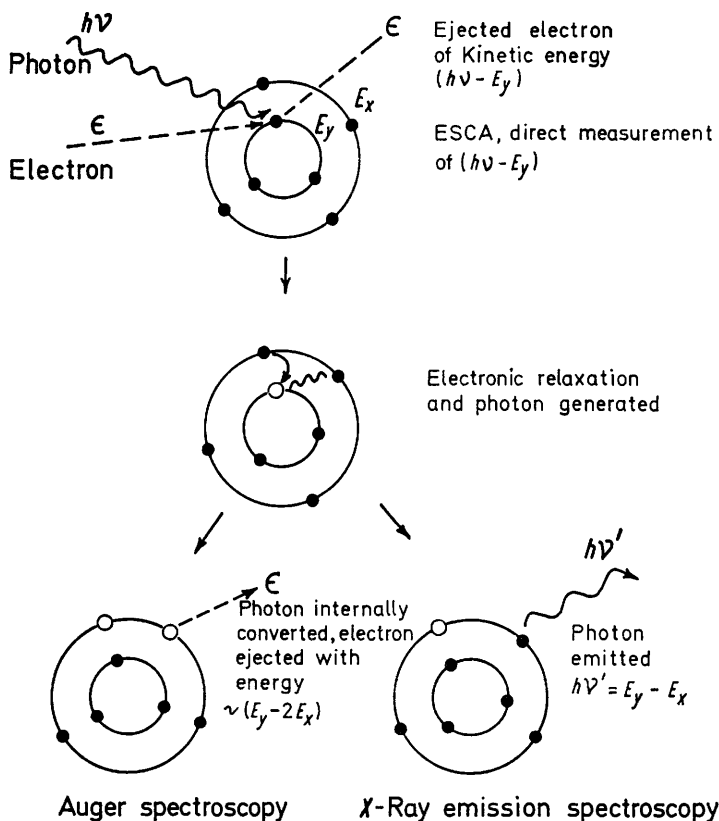


Figure 2

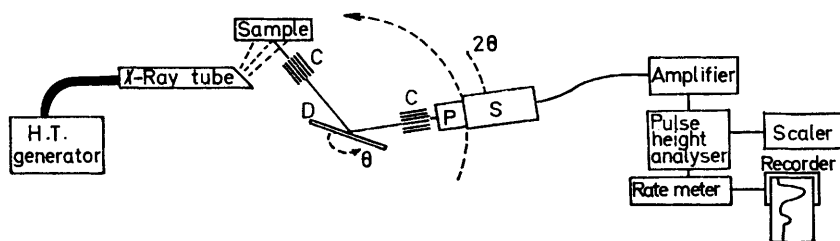
⁴ P. Auger, Thesis, Paris, 1926; E. H. S. Burhop, 'The Auger Effect', Cambridge University Press, Cambridge, 1952.

If atoms are irradiated with mono-energetic electrons or *X*-rays then not only will vacancies be generated and characteristic *X*-rays observed but it will be possible to measure the binding energy of the ejected electron since, to a first approximation, the kinetic energy of the emitted electron will equal the energy of the incident electron or photon less the binding energy. This is the basis of electron energy spectroscopy, also known as ESCA⁵ (electron spectroscopy for chemical analysis) or IEE (induced electron emission) spectroscopy.

The three spectroscopies *X*-ray emission, Auger, and electron emission are complementary. The fundamental processes are summarised in Figure 2. Electron energy spectroscopy provides information about orbital ionisation energies whereas *X*-ray emission spectroscopy measures energy differences between inner and less tightly bound orbitals. Auger spectra give 'hybrid' data, since an *X*-ray emission quantum has initiated photo-electron emission. Because valence shell atomic orbitals are perturbed in energy by chemical bond formation and because ionisation energies of inner atomic orbitals are sensitive to charge distributions in valence orbitals, effects due to chemical bonds can be observed in all three spectroscopies. These effects are manifest as variations in energies and numbers of emitted photons or electrons. In actual experiments where results are usually displayed as intensity of emission *vs.* energy of emission these effects give rise to peak shifts, variations in peak intensities, and the formation of new peaks. Current interest in electron energy⁵ and Auger⁶ spectroscopies has produced considerable literature on these subjects so this review will emphasise the strangely neglected, chemical potential of *X*-ray emission spectroscopy.

2 Apparatus

The essential features of an *X*-ray spectrometer are: (1) an excitation source with which to irradiate the sample, (2) a means of analysing the emitted radiation



C = collimator , D = diffracting crystal , P = proportional counter
S = scintillation counter

Figure 3 *X*-Ray fluorescence spectrometer. As the diffracting crystal moves through an angle θ , the counters move through an angle 2θ

⁵ K. Siegbahn *et. al.*, *Nova Acta Regiae Soc., Sci. Upsaliensis*, 1967, Ser. IV, 20, 1; 'ESCA Applied to Free Molecules', North-Holland Pub. Co., Amsterdam, 1969.

⁶ J. C. Riviere, *Inst. Phys. and Phys. Soc. Bull.*, 1969, 20, 85.

with respect to frequency, and (3) a means of detecting and measuring the intensity of the radiation.

In a conventional *X*-ray fluorescence (XRF) spectrometer (Figure 3), (1) is an *X*-ray tube, (2) is a suitable crystal, and (3) is a proportional or scintillation counter, depending upon the wavelength of the radiation to be detected. Air can be tolerated between the various parts of the spectrometer if hard *X*-rays ($\lambda < 0.2$ nm) are being studied, but for softer *X*-rays ($0.2 \text{ nm} < \lambda < 0.5 \text{ nm}$) the whole apparatus must be flushed with helium. For soft *X*-rays ($\lambda > 0.5 \text{ nm}$) a vacuum within the spectrometer is essential.

In an *X*-ray tube a beam of electrons is accelerated at a target made of a suitable metal, *e.g.* chromium, molybdenum, copper, silver, tungsten, *etc.* The target will emit its own *X*-rays and also a considerable amount of white radiation, *i.e.* radiation spread over a wide wavelength range with a fairly homogeneous intensity. Now, the efficiency with which a particular element can be stimulated to emit *its* own characteristic radiation varies with the irradiating frequency so that a variety of *X*-ray tubes is necessary in order to ensure the optimum conditions for the detection of any particular element that may be present in a sample. Sometimes complications can arise because of similarities in the emission frequencies of the *X*-ray tube and the sample, in which case a different source of excitation should be used.

The sample is placed as near to the *X*-ray tube as possible so that the maximum intensity will fall upon it. The radiation emitted by the sample passes through a collimator and falls upon a suitable crystal. Here the *X*-rays are diffracted according to the Bragg equation:

$$n\lambda = 2d \sin \theta$$

n = order of diffraction, *i.e.* 1, 2, 3, *etc.*

λ = wavelength of radiation

d = distance between two diffracting planes in the crystal

θ = angle of incidence, angle of diffraction of radiation relative to the diffracting planes.

A list of commonly used crystals is given in the Table. For long *X*-ray wavelengths (> 5 nm) a diffraction grating is the most accurate method of dispersing radiation. By the use of suitable gratings any wavelength range can be studied up to and including the vacuum u.v. (> 100 nm). The convenience of the crystal spectrometer is such that materials have been produced with very large $2d$ spacings, up to 16 nm.

As can be seen from the equation above there is the possibility of multiple-order diffraction; this can cause considerable confusion in the interpretation of results unless it can be eliminated. The introduction of modern methods of photon detection has considerably simplified this problem since the height of the pulse (in mV) given out by the scintillation or proportional counter is directly related to the energy of the incident ray. The energy of radiation of a particular frequency will be the same whether it suffers first-, second- or third-, *etc.* order diffraction. Pulse height analysis techniques may, therefore, be used to select just the energy

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that corresponds to the order diffraction that is required and to eliminate spurious signals from other orders. The use of pulse height analysis in this way also serves to improve the signal-to-noise ratio by reducing background.

The scintillation counter is often placed directly behind the proportional counter so that soft *X*-rays may be detected by the latter but hard *X*-rays will pass straight through the proportional counter to be detected only by the scintillator. In this way a wide range of possible *X*-ray energies can be detected in a simple and compact way. Many refinements of this basic system are, of course, possible and improvements are continually being made. Typical commercial instruments are produced by Philips, Siemens, Hilger and Watts, and General Electric.

A simplification of the standard XRF spectrometer utilises to the full the proportional character of modern photon detectors. Solid state devices⁷ in particular are capable of resolving photon energies only a few hundred electron volts apart, down to a lower limit of detection of about 5 keV. The dispersing crystal can be omitted (this also eliminates the problem of multiple-order diffraction) and the characteristic *X*-rays are analysed directly they leave the sample. Such a non-dispersive *X*-ray spectrometer is shown in Figure 4. The

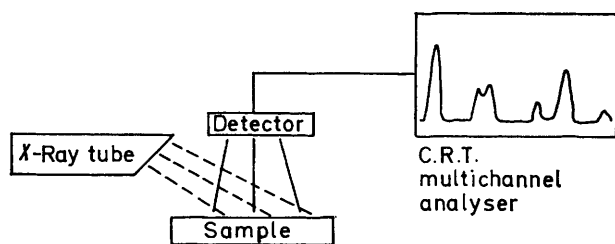


Figure 4 Non-dispersive X-ray emission spectrometer

spectrometer can be simplified even more if the *X*-ray tube, or electron gun, is replaced by a powerful radioactive source.⁸ In this form an XRF spectrometer becomes a portable hand instrument for the immediate analysis of geological samples in the field.

Another type of *X*-ray spectrometer utilises accelerated electrons to stimulate characteristic *X*-ray emission from a sample. The main advantage is that the electron beam can be focused onto a very small area [$1 \mu\text{m}^2$] of sample and also that the beam can be made to scan over the sample. In this way a detailed analysis of a heterogeneous specimen can be carried out. This type of instrument is the Electron Beam Microprobe. If the spectrometer is set to detect a particular element then the results of the scan over a specimen can be presented pictorially on a cathode ray tube; bright areas indicating the presence of the element,

⁷ T. W. Haas, J. T. Grant, and G. J. Dooley, *Phys. Rev. (B)*, 1970, 1, 1449.

⁸ J. R. Rhodes, *Analyst*, 1966, 91, 683.

dark areas its absence. This technique has very wide application in the study of rock samples, corroded surfaces, biological specimens, *etc.* The 'Betraprobe' (Telsec Ltd.), whilst using electrons to cause the emission of characteristic X -radiation, is more similar to a conventional X -ray spectrometer since the electrons fall evenly over a sample of about 1—5 cm². This apparatus has the advantage over spectrometers using X -irradiation that more intense characteristic radiation from light elements is produced. However, as with the electron microprobe it is necessary to have a conducting sample (or if the sample is the insulator it is necessary to cover the sample with a very thin layer of a conducting substance) and to work under high vacuum conditions ($\sim 1 \mu\text{Torr}$).

The instruments described above generally function in the wavelength range 50—1000 pm. This covers the analytically useful characteristic emissions of all the elements with atomic numbers greater than 12 (Mg). This range can be extended without much difficulty to 2.6 nm, thus including the elements sodium to oxygen. However, the intensity of X -ray emission falls off rapidly with decreasing atomic number for elements in this part of the periodic table so that considerable difficulty is encountered in detecting the lighter elements. The soft X -ray region corresponding to long X -ray wavelengths ($> 0.5 \text{ nm}$) and relatively low energies ($< 2000 \text{ e.v}$) is one of considerable potential importance to chemists. X -Ray transitions from the valence shell to a vacancy in an inner orbital will often show variations in frequency and intensity due to chemical bond formation. These variations are often of a few electron volts and can be fairly easily observed in peaks of less than, say, 2000 e.v. For peaks of much greater energy the percentage energy change caused by chemical effects is increasingly difficult to detect. The problems associated with work in this region are, typically, low intensity of signal, difficulty of detecting low energy photons, and choice of a suitable diffracting crystal. These may be overcome by using a high intensity source at a long wavelength (*e.g.* Al $K\alpha$ 833.9 pm or Cu L 1336 pm), by using very thin windows in a proportional counter which is itself operated at about $1/3 \sim 1/10$ of atmospheric pressure, and by the development of 'soap film' crystals or the use of gratings.

A study of the energies of photo and Auger electrons^{5, 6} emitted by atoms as a result of irradiation by monoenergetic X -rays is complementary to X -ray emission spectroscopy. Whilst it should in principle be possible to combine X -ray emission and electron energy spectroscopies into a single instrument, utilising a single X -irradiation source, this has not yet been attempted. The fundamental features of an electron energy spectrometer are indicated in Figure 5. It is essential that monoenergetic radiation (frequency ν) be used since the energies of the emitted electron (E_K) depend upon the following relationship:

$$E_K = h\nu - E_b - C$$

E_b = binding energy of electron

C = work function constant for sample and spectrometer

Uncertainty in ν is therefore directly transmitted to uncertainty in E_b . The aluminium $K\alpha$ line, which has been extensively used, has a natural line width of

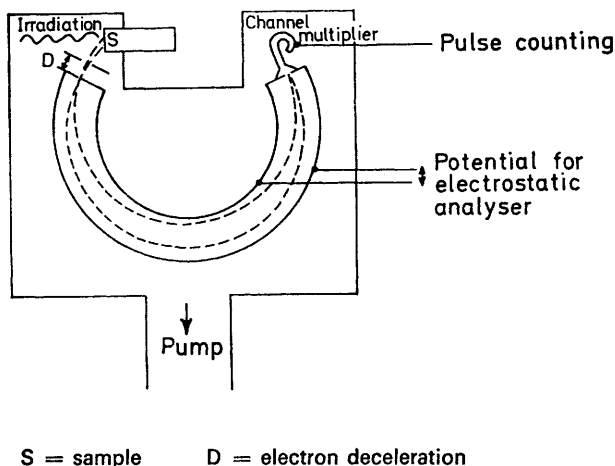


Figure 5 Electron energy spectrometer using electrostatic analysis (electron paths shown as dashed lines)

about 1 eV, and this is quite acceptable for the determination of electron binding energies of greater than about 100 eV. For valence shell molecular orbital binding energies the much lower helium resonance line radiation (21.12 eV) has been used. The narrow line width enables very much greater resolution of energy levels, not just of molecular orbitals, but of vibrational (and even in exceptional cases, rotational) states to be found. Since the energies of the electrons being detected in electron spectrometers are so low it is essential to exclude all possible variations in magnetic field. For electrostatic analysers small metal shields are usually quite adequate, although extensive Helmholtz coil systems are sometimes used. If a wide range of electron energies is to be determined a deceleration stage is often included before the analyser. The electrons that emerge from the energy analyser are usually detected by an electron multiplier and the signals so generated are counted using conventional pulse counting equipment.

3 Experimental Results

X-Ray fluorescence spectroscopy is most widely used in analysis^{8,9}. For all elements, save the lightest, it is possible to find X-ray emissions of suitable intensities and at convenient frequencies. This permits the qualitative detection of many elements in trace amounts of only a few parts per million. The use of XRF in quantitative analysis and in establishing accurate element ratios is

⁸ L. S. Birks, 'X-Ray Spectrochemical Analysis', Interscience, J. Wiley, New York, 2nd. edn. 1969; R. Jenkins and J. L. de Vries, 'Practical X-Ray Spectrometry', MacMillan, London, 2nd. edn., 1970; H. A. Liebhafsky, H. G. Pfeiffer, E. H. Winslow, and P. D. Zemany, 'X-Ray Absorption and Emission in Analytical Chemistry', Wiley, New York, 1960.

rather more difficult, since many factors conspire to attenuate or enhance some of the emission intensities. These factors can include self-absorption, the formation of chemical bonds, the specific presence of other elements, the physical size of the particles of the sample, *etc.* Even so, XRF spectroscopy can be successfully used quantitatively in cases where chemical composition, particle size, *etc.* can be controlled, *e.g.* glass, cement, ceramics, iron and steel, slags, and many other minerals, *etc.*

From the chemist's point of view the changes that take place in peak shape are of greater interest since the changes are directly related to chemical effects such as bond formation. In metals or alloys transitions between inner orbitals give rise to sharp symmetrical peaks but a transition from a valence orbital to an inner vacancy is often distorted or exhibits complex structure (Figure 6).

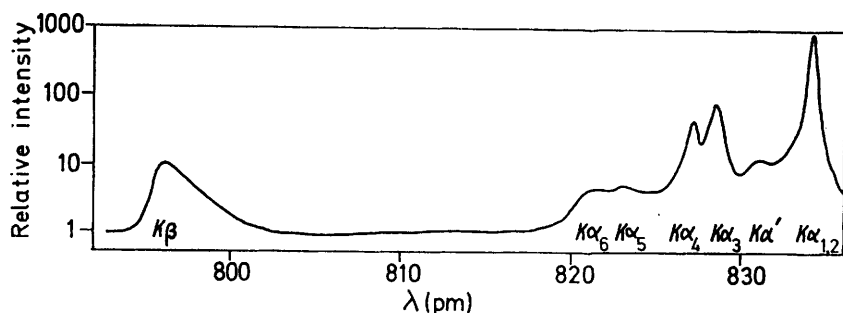


Figure 6 X-Ray emission spectrum of metallic aluminium. Vertical scale, of relative intensity, is logarithmic. Note the symmetrical shape of the $K\alpha_{1,2}$ peak and the distorted shape of the $K\beta$ peak. The other $K\alpha$ peaks are due to emissions from doubly ionised atoms

The reason for the difference in shape is the participation of the valence orbitals in delocalised bond formation. Indeed, it is possible to use such X-ray emission data as a check on the accuracy of theoretical calculations on the orbital band structure of metals and alloys¹⁰.

When the spectra of pure metals and their compounds are compared it is usually found that those peaks that were distorted in the metal are quite symmetric in chemical compounds (Figure 7). This is because those orbitals that were participating in a very extensive and delocalised set of orbitals are now making only a few simple localised bonds. A particular atomic orbital will be present in only a few molecular orbitals. There should be just a few transitions corresponding to these orbitals. (A broad, distorted peak may be thought of as being due to transitions from many orbitals very closely spaced in energy—the shape of a distorted peak is then a function of the particular atomic orbital's degree of participation in each molecular orbital and the density of such orbitals on an energy scale). Even with the resolution of conventional instruments it is

¹⁰ 'Soft X-Ray Band Spectra', ed. D. J. Fabian, Academic Press, London, 1968.

usually possible to detect all these transitions. Typically, there will be one main peak and new peaks which are called satellite peaks (Figure 7). Those

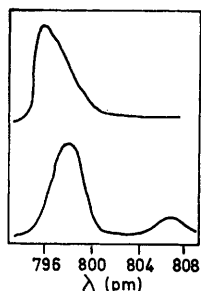


Figure 7 $K\beta$ emissions from aluminium; top curve, metallic aluminium; lower curve, alumina (peak at ~ 806 pm is designated $K\beta'$)

satellite peaks that are specifically associated with chemical bond formation are usually of lower energy than the main peak. High energy satellite peaks are also observed both in pure elements and their compounds (Figure 8). These emissions are derived from transitions in doubly ionised atoms, the theory of which is well understood.¹¹

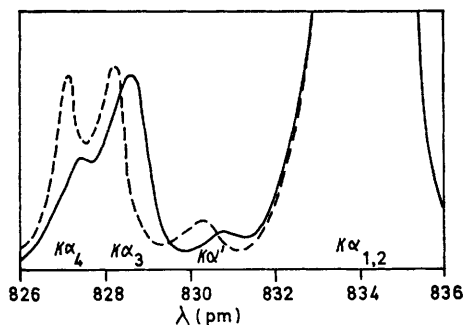


Figure 8 Detail of fine structure of $K\alpha$ high-energy satellites from aluminium; solid line, aluminium metal; dashed line, alumina

Besides the formation of new satellite peaks and the changes in peak shape that occur when chemical bonds are formed the actual wavelength of the main peak itself can also be changed slightly. This is referred to as 'peak shift' (Figure 7). Transitions from valence orbitals give rise to peaks which can be

¹¹ F. R. Hirsch, *Rev. Mod. Phys.* 1942, 14, 45; D. J. Candlin, *Proc. Phys. Soc.*, 1955, A68, 322.

altered in shape, wavelength, and intensity by bond formation. A careful study of the way in which these three factors vary from compound to compound can be of great value in analysis, in structural studies, and in comparison with theoretical calculations. Although it is very reasonable that transitions from outer orbitals should reflect chemical effects, X-ray emissions between inner, non-valence orbitals are also subject to 'peak shifts'. The energy changes in these 'inner orbital shifts' are less than those involving valence shells but, because inner orbital transitions often give rise to more intense emissions and sharper peaks, they are equally important in establishing correlations between peak shifts and coordination number or peak shift and bond length. Day¹² has shown that the exact wavelength of the $K\alpha$ emission from aluminium can be correlated with either four-fold or six-fold co-ordination (Figure 9). And Gibbs and White¹³

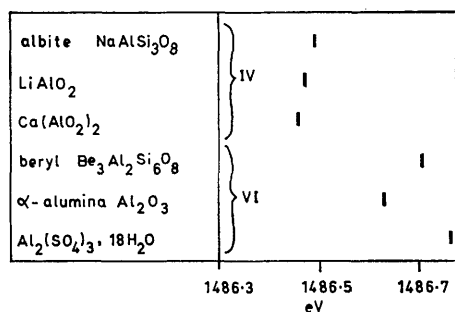


Figure 9 Aluminium $K\alpha$, showing the relationship between aluminium co-ordination number and $K\alpha$ transition energy (data from ref. 12)

have shown how displacement of the $K\beta$ peak of aluminium or silicon can be related both to co-ordination number and to bond lengths (Figure 10). Such empirical correlations are obviously of great value in chemistry.

So far only typical emission spectra have been discussed; this is because such spectra are readily available. Of equal interest and of complementary value are absorption spectra. These are more difficult to obtain because of the requirement that the specimen be in the form of a *very* thin plate of film. Absorption spectra are important, not only in their own right but also so that the self-absorption of a sample can be observed. In compounds with completely filled, or empty orbitals the emission wavelengths will be different from those for absorption but where partly filled orbitals are present (as in transition metal and rare-earth compounds) some overlap of absorption and emission wavelengths must be anticipated. Such self-absorption might give rise to curious structure

¹² D. E. Day, *Nature*, 1963, **200**, 649.

¹³ E. W. White and G. V. Gibbs, *Amer. Mineralogist*, 1967, **52**, 985; *ibid.*, 1969, **54**, 931.

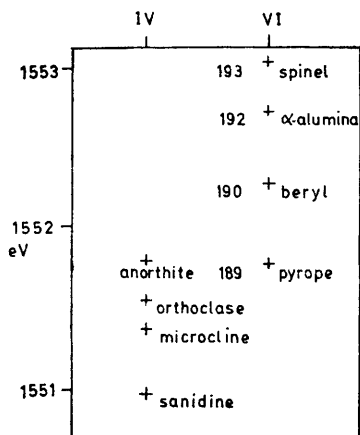


Figure 10 Aluminium $K\beta$, showing the relationship between aluminium co-ordination number and $K\beta$ transition energy. Al-O bond lengths (pm) are indicated for the six-co-ordinate compounds showing that this factor is also related to the position of the $K\beta$ peak

in the emission spectrum. This was clearly demonstrated by Fischer and Baun¹⁴ in their studies of the $M\alpha$ and $M\beta$ emission spectra of a series of lanthanides. As can be seen from Figure 11 the original emission spectrum is quite complex. The 'fine structure' is, however, all due to self-absorption; when this has been taken into account the true emission spectrum is seen to be quite simple and straightforward. In the absence of complementary absorption studies there is the danger of quite elaborate explanations of 'emission fine structure' being made, which would be completely spurious.

From the chemical point of view those absorptions which are of most interest are those which involve transitions to antibonding molecular orbitals. The peak shifts, intensity changes, *etc.* that are observed in absorption should be complementary to those found in emission.

A limit to the detail that can be observed in both absorption and emission spectra is set by the natural line widths of the peaks that are observed and the resolving power of the instrument. Line widths will be determined by the lifetime of the excited state¹⁵ but are typically about 1 eV. The resolving power of a crystal spectrometer is a function of the angle of diffraction, being greatest when θ is large. For best resolution, therefore, spectra should be taken at large θ angles. This can be achieved by having a wide range of dispersing crystals available and by the occasional use of higher-order diffractions.

These natural and experimental factors put a limit to the complexity of a spectrum that can be successfully resolved. Clearly complex compounds with

¹⁴ D. W. Fischer and W. L. Baun, *J. Appl. Phys.*, 1967, **38**, 4830.

¹⁵ D. J. Nagel, *Adv. X-Ray Anal.*, 1970, **13**, 182 (Appendix 1, Decay of X-Ray States, p. 217).

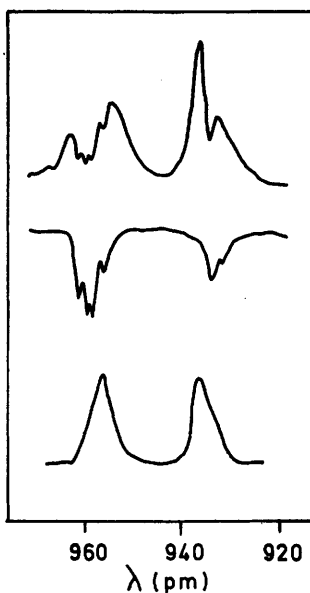


Figure 11 Top curve: $M_{\alpha,\beta}$ emission spectrum of dysprosium; middle curve: absorption spectrum of dysprosium; bottom curve: $M_{\alpha,\beta}$ emission of dysprosium under conditions of negligible self-absorption

many closely spaced orbitals will give broad undulating spectra without a clear resolution of peaks that could be correlated with particular orbitals. Simple, well resolved spectra will be obtained from molecules where there are not many atoms of the same element in different bonding situations (*e.g.* sulphur in S_8 would be easier to interpret than carbon in C_3H_8).

4 Molecular Orbital Model

The simplest model for the bonding in a chemical compound which describes the degree of participation of atomic orbitals in various molecular orbitals is that derived from molecular orbital theory.¹⁶ Even in its simplest, most approximate form it enables a framework of molecular orbitals to be constructed for any molecule, it enables orbital energies to be calculated, and it estimates, by an evaluation of LCAO coefficients, the amount of each atomic orbital to be found at each atom in every molecular orbital.

By way of example, consider the MO model for a tetrahedral arrangement of four ligand atoms L about a central atom X, utilising the symmetry of the system to simplify the calculations.¹⁷ The array of molecular orbitals that will be

¹⁶ C. A. Coulson, 'Valence', Oxford University Press, Oxford, 1952; J. D. Roberts, 'Notes on Molecular Orbital Calculations', Benjamin, New York, 1962; J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, 'Valence Theory', Wiley, London, 1965.

¹⁷ D. S. Urch, 'Orbitals and Symmetry', Penguin Education, London, 1970; F. A. Cotton, 'Chemical Applications of Group Theory', Interscience, Wiley, New York, 1964.

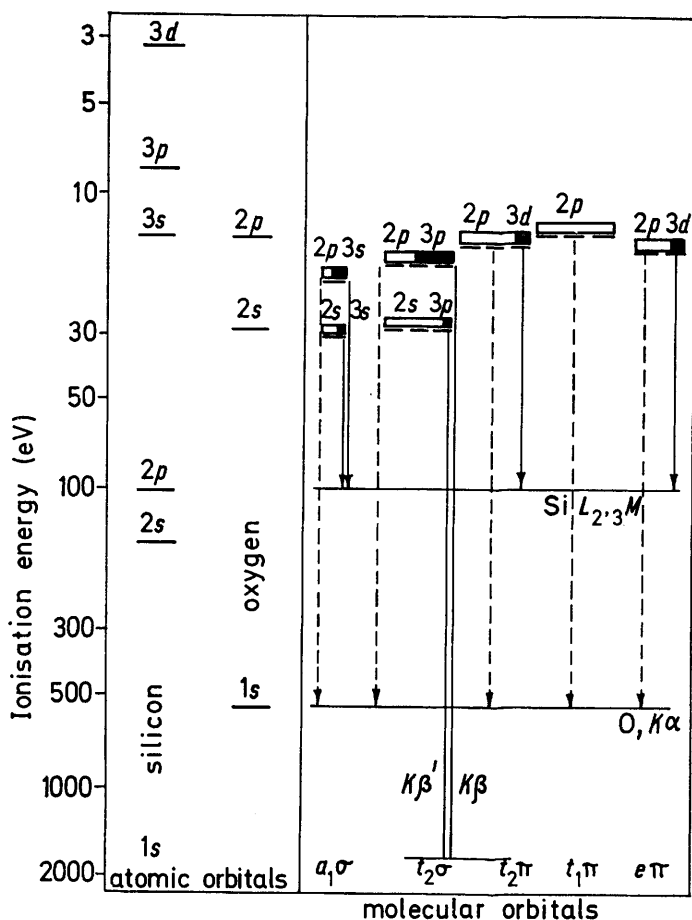


Figure 12 Molecular orbital energy level diagram for a tetrahedral complex such as SiO_4 . Possible X-ray transitions for oxygen are shown as dashed lines, those for silicon as solid lines. The vertical scale is logarithmic. No interaction between $t_2\sigma$ and $t_2\pi$ has been considered

formed is shown diagrammatically in Figure 12. As the energies of ligand and central atom orbitals change, so will the MO energies and also the relative amounts of the various atomic orbitals present in each MO. The ordering of the orbitals shown in Figure 12 can be applied to oxygen ligands surrounding an atom such as aluminium or silicon. As can be seen, a central atom orbital such as 3s, which in the free atom would be involved in a transition to a 2p vacancy giving rise to a single peak split only by spin orbit coupling, participates in occupied molecular orbitals of two distinct energies. A vacancy in a 2p orbital will, therefore, attract transitions from all the molecular orbitals with 3s character.

The energy (*i.e.* wavelength) of the transitions will reflect the ionisation energy differences between the molecular orbital and the $2p$ orbital and the intensities of the transitions will be determined by the amount of $3s$ character in the MO and also by the number of electrons. There is, therefore, a direct relationship between transition intensity and the coefficients found in the LCAO equations.

A diagram of the type shown in Figure 12 can be used to interpret all the observed features of an X -ray emission spectrum.^{18,19} The formation of satellite peaks when bonds are made is due to atomic orbitals participating in more than one molecular orbital. The first theory²⁰ of satellite peaks suggested a 'cross-over' from a ligand atom to the central atom vacancy but the intensity of such a transition would be very much less than is observed.¹⁸ Often the energy of separation between the main peak and a low energy satellite (*e.g.* $K\beta \sim K\beta'$) can be related to the $2s-2p$ ionisation energy difference of the ligand. This energy difference therefore has a diagnostic value in analysis. It can be used to identify the chemical nature of a ligand atom. Provided the systems are not too complex, a study of satellite peaks can thus provide structural as well as merely analytical information.

Whilst this molecular orbital model provides a sample qualitative framework for a discussion of the origin of satellite peaks and the variations of peak intensity it can only provide half the explanation for peak shifts. An emission spectrum results from a transition between two orbitals, and the inner orbital will also be subject to chemical bond effects.⁵ Changes in the ionisation energies of inner shell orbitals seem to be directly related to the effective charge on the atom. Valence shells have small but important amplitudes in the same regions of space as inner shell orbitals. Electron repulsion terms of some significance will, therefore, exist between inner and outer orbitals. Variations in electron population or orbital amplitude of the valence shell orbitals due to chemical bond formation will, therefore, cause changes in these repulsion terms and, thus, in the ionisation energies of inner orbitals. In general, as an atom becomes more positively charged so the ionisation energies of inner orbitals increase. All other things being equal this would cause an X -ray emission peak to shift to higher energies (shorter wavelengths). However, other things are far from equal since the valence shell molecular orbital energies will also vary—both as a function of the ionic character of a bond and as a function of the type of ligand. All these factors conspire to make the theoretical interpretation of peak shifts rather difficult. A direct determination of inner orbital energies by the ESCA technique is invaluable in any attempt to unravel the causes of peak shifts.

It is interesting to notice that in many cases the energy of a particular peak, say Si $K\beta$, is surprisingly invariant as ligands are changed.²¹ This is because of two parallel effects acting on valence shell and inner shell orbitals. As the ligand electronegativity increases so does the ionisation energy of the corresponding

¹⁸ D. S. Urch, *J. Phys. (C)*, 1970, **3**, 1275.

¹⁹ C. G. Dodd and G. L. Glen, *J. Appl. Physics*, 1968, **39**, 5377.

²⁰ H. M. O'Brien and H. W. B. Skinner, *Proc. Roy. Soc.*, 1940, **A176**, 229.

²¹ D. S. Urch, submitted for publication, *J. Phys. Radium*, 1971.

molecular orbital. However, the increase in ligand electronegativity will also enhance the effective positive charge on the central atom so that inner orbital ionisation energies will also be increased. The two increments are often very similar so that the $K\beta$ peak suffers a shift of less than two electron volts when the ligands are changed, nitrogen to oxygen to fluorine.

Greater peak shifts can be caused by a deliberate manipulation of the central atom charge with a constant set of ligands. This may be achieved either by altering the ionic character of bonds²² (by altering bond lengths, and co-ordination number) or the formal valency of the central atom.²³

5 Application of X-Ray Emission Spectroscopy in Chemistry

A. Theoretical Chemistry.—The intensity of electromagnetic dipolar emission is governed by the square of a function of the type, $A\nu^3 \int \psi_I \mathbf{P} \psi_{II}$,²⁴ where A stands for a collection of constants, ν is the frequency of the emission that results from an electronic transition between the two states whose wave functions are ψ_I and ψ_{II} , and \mathbf{P} is the operator function which effects the transition. If an atomic orbital (ϕ) from atom R participates in two molecular orbitals (ψ_1 and ψ_2) it will do so with coefficients a_{1R} and a_{2R} at atom R. When a vacancy is made in an inner orbital which would permit a transition from ϕ this transition will occur whether R is chemically bound or not, but the intensity will change. For the free atom the function above would be $A\nu^3 \int \psi_I \mathbf{P} \phi$ but in the chemical compound two peaks would be observed and the function would have the values $A\nu^3 \int \psi_I \mathbf{P} (a_{1R} \phi)$ and $A\nu^3 \int \psi_I \mathbf{P} (a_{2R} \phi)$. If wavelength shifts are relatively small so that ν is effectively constant then the relative intensities would be (if the number of electrons in each orbital is the same), peak for free atom: peak in compound: satellite peak in compound = $1 : (a_{1R})^2 : (a_{2R})^2$.

Unfortunately, there is no data of absolute emission intensity for free atoms. It is necessary to use, as best one can, data from pure elements. For this purpose the $K\alpha : K\beta$ intensity could also be used for second row elements. If it is assumed that the $K\alpha$ intensity is not affected by chemical combination then it can be used as a reference standard in comparing elements and their compounds. If the $K\alpha : K\beta$ ratio increases then it shows the electron population in the orbitals giving rise to $K\beta$ has also increased. Arguments of this type can give a good deal of insight into the nature of the chemical bond.^{18, 25} Thus, in alumina it would be readily agreed that the Al—O bond should be polar and that electron donation should take place from alumina to oxygen, yet X-ray emission data shows that the $K\alpha : K\beta$ ratio increases on oxidation indicating an *increase* in electron density, not a decrease, near the aluminium.²⁶ This is, of course, only in the $3p$ orbitals.

²² D. S. Urch, to be published, *Proc. 7th. X-Ray Anal. Conf.*, Durham, 1970.

²³ D. W. Wilbur and J. W. Gofman, *Adv. X-Ray Anal.*, 1966, **9**, 354; M. A. Blokhin, T. T. Shubaev, and V. V. Gorskii, *Izvest. Akad. Nauk. S.S.S.R., Ser. Fiz.*, 1964, **28**, 801 (p.709, Eng. Trans).

²⁴ H. Eyring, J. Walter, and G. E. Kimball, 'Quantum Chemistry', Wiley, New York, 1944.

²⁵ A. T. Subaev, *Izvest. Akad. Nauk. S.S.S.R., Ser. Fiz.*, 1961, **25**, 968 (Eng. Trans., **25**, 996).

²⁶ D. W. Fischer, *Adv. X-Ray Anal.*, 1970, **13**, 159.

Very simple MO calculations¹⁷ in fact, show that the greatest donation is to be expected from the $3s$ orbitals; there is apparently some back donation *via* molecular orbitals that have $3p$ character. The investigation of relative peak intensity in this way also opens up the possibility of a direct experimental determination of charge distribution in bonds, which can then be correlated with dipole moments and possibly with chemical reactivity, and the direct determination of LCAO coefficients. If s orbital coefficients can be found using this method this data could be used to estimate nuclear coupling constants and a relationship established with nuclear magnetic resonance data. s Orbital densities are also relevant to Mössbauer data, and so details of the charge distribution as a function of orbital type should help considerably in interpreting Mössbauer spectra. Nuclear quadrupole effects are primarily due to field gradient changes in p orbitals and as such this spectroscopy can be used to probe charge variations in p orbitals in a series of homologous compounds. A comparable study of relative X -ray emission intensities should provide analogous data which could be used to confirm the n.q.r. results.

One of the simplest rules that can be applied to the interpretation of X -ray emission spectra is $\Delta l = \pm 1$ ($l =$ atomic orbital azimuthal quantum number), *i.e.* an s vacancy can be filled only by an electron from a p orbital; p vacancy, s or d orbitals; d vacancy, p or f orbitals, *etc.* X -Ray emission spectroscopy therefore provides the chemist with a most exciting technique to probe orbital participation in bond formation. Since a p vacancy can be filled only from molecular orbitals with s or d character it is quite possible in symmetric circumstances, to point to particular peaks (in this case 'high-energy' satellites) as proof that d orbitals do have a bonding role in some of the compounds of main group elements²⁷. Data is only available for a few oxyanions but clearly this method could be easily used as a diagnostic test for the presence of d character in the bonds of any compound, thus ending years of speculation and conjecture. The method could, in principle, be extended to other related problems, *e.g.* do the elements tin, antimony, tellurium *etc.* use $4f$ or $5d$ orbitals, or both or neither?

B. Inorganic Chemistry.— X -Ray emission spectroscopy has been most widely used for the analysis of inorganic compounds, and so most detailed work on chemical effects has been done in this field. Rock forming minerals have been particularly well studied and correlations between co-ordination number and peak shift, mentioned above, and also between bond lengths and peak shift, have been established. For aluminium and silicon the formal oxidation number does not change but in a series of sulphur compounds, for example, it does.²³ Peak shifts can then be correlated with the formal charge or oxidation state.

Up to now the principal physical use of X -ray emission spectra has been to determine the band structure of solids. Attempts, usually quite successful, have been made to correlate the observed spectra with theoretical calculations and with physical properties. Besides the compounds of main group elements

²⁷ D. S. Urch, *J. Chem. Soc. (A)*, 1969, 3026.

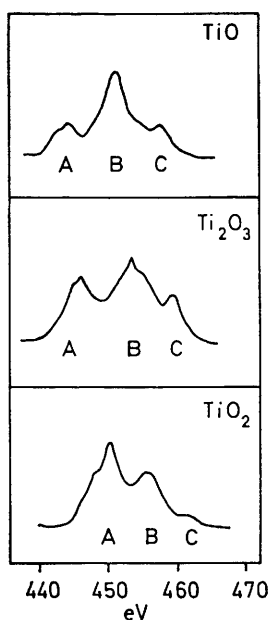


Figure 13 Titanium $L_{2,3}M$ spectra from titanium oxides

mentioned in previous sections, a considerable number of transition metal compounds have been studied. Vanadium and titanium in combination with carbon, nitrogen, and oxygen have been particularly thoroughly studied by Fischer and Baun.²⁸ Ti $L_{2,3}M$ emission spectra for TiO , Ti_2O_3 , and TiO_2 are shown by way of example in Figure 13. Peaks B and C are due to the anticipated Ti $3d \rightarrow 2p$ transition, split by spin-orbit coupling of the $2p$ vacancy. A is the low energy satellite associated with bond formation to the ligand oxygen. A is the satellite to B but the corresponding satellite to C is unresolved from B. What are most interesting are the changes in relative intensity between A and B and C as the formal oxidation of titanium increases. The somewhat covalent character of the TiO_2 bond in rutile is clearly shown by the continued presence in the spectrum, of peaks B and C. In order to obtain a more detailed understanding of the bonding in these compounds the corresponding absorption spectra as well as oxygen $K\alpha$ spectra were also recorded. But for a complete picture the Ti, K spectra should be determined and relative peak intensity variations investigated.

A careful thorough study of spectra of a variety of known compounds should permit qualitative rules to be established which would enable oxidation state and co-ordination number to be determined for any atom in a compound. In many cases the chemical nature of ligand atoms might also be established from studies of satellites.

²⁸ D. W. Fischer and W. L. Baun, *J. Appl. Phys.*, 1968, **39**, 4757; *ibid.*, 1970, **41**, 3561.

C. Organic and Organometallic Chemistry.—The energies of the characteristic X -rays of the first row elements are all less than 1000 e.v. (*i.e.* > 1.24 nm). Being weak the X -rays are readily absorbed; their detection is therefore difficult. Suitable crystals with large $2d$ spacings have been found so that diffraction is no longer a problem. Proportional counters may still be used to detect these very soft X -rays but very thin windows must be used and, of course, a good vacuum established within the spectrometer. Some workers use a reduced gas pressure within the proportional counter to reduce the stress on the thin window. With care the difficulties of long-wavelength work can be overcome; the

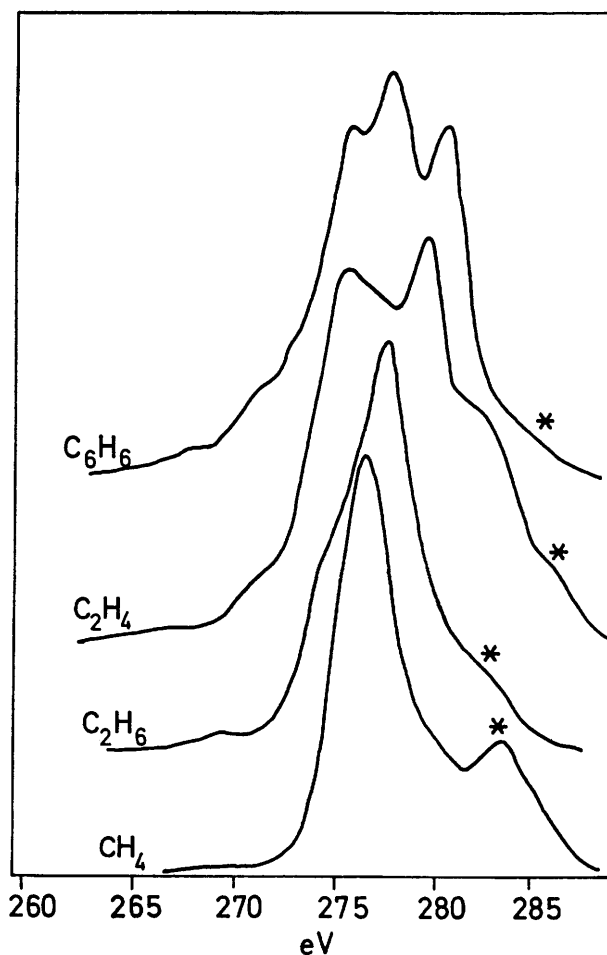


Figure 14 Carbon $K\alpha$ emission spectra from hydrocarbon gases. Peaks marked * are probably due to transitions in doubly ionised species

major difficulty, however, remains that of generating the X-rays in the first place. It is an unfortunate fact of nature that the probability for a photon to be internally converted increases as atomic number decreases, *i.e.* at low atomic number the characteristic X-ray photon tends not to leave the atom but rather it is consumed in ionising an electron (Auger effect). In order to detect an X-ray emission from light elements it is, therefore, necessary to have a very powerful source of suitable X-rays. Special X-ray tubes giving prolific emission of Cu *L*, or Al *K* α radiation (power about 4 kW) have been developed by Henke²⁹ but are not yet (1970) commercially available.

The spectra that could be obtained from organic compounds would be of the greatest interest since the results would probe the bonding involvement of carbon *2p* orbitals (because the only possible emission transition is *2p* \rightarrow *1s*). The results of Mattson and Ehlert³⁰ for some simple hydrocarbon gases are shown in Figure 14. The high-energy peak may be ignored since it is a transition in a doubly ionised species but the other peaks show how *2p* orbitals contribute to various molecular orbits. A most satisfactory correlation with MO calculations has been given by Manne.³¹ This work clearly shows the potential importance of X-ray fluorescence spectroscopy in organic chemistry. This potential is probably even greater in organometallic chemistry where the bonding involvement of a wide variety of orbitals, both ligand and metal, could be determined. Unfortunately, no detailed investigation of an organometallic compound has yet been carried out.

6 Conclusion

X-Ray fluorescence spectroscopy has still to be applied to a wide spectrum of chemical compounds; yet its potential for providing information of chemical interest and importance would seem to be enormous. The applications can be summarised as follows:

- (i) element analysis; qualitative and, in favourable cases, quantitative
- (ii) structural analysis; identification of neighbouring atoms, determination of co-ordination number, sometimes bond length
- (iii) determination of oxidation state
- (iv) study of bonding role of atomic orbitals

Sometimes the information that can be obtained merely confirms that from other analytical techniques, sometimes the information complements that from other spectroscopic methods but in many cases quite unique information is discovered. It therefore seems reasonable to expect that X-ray emission spectroscopy will at last join the ranks of those spectroscopic methods that have transformed our understanding of chemistry during the past twenty years.

²⁹ B. Henke, *Adv. X-Ray Anal.*, 1962, **5**, 285; *ibid.*, 1963, **6**, 361; *ibid.*, 1964, **7**, 460; *ibid.*, 1966, **9**, 430; J. A. Dunne and W. R. Muller, *Develop. Appl. Spectroscopy*, 1965, **4**, 33.

³⁰ R. A. Mattson and R. C. Ehlert, *J. Chem. Phys.*, 1968, **48**, 5465.

³¹ R. Manne, *J. Chem. Phys.*, 1970, **52**, 5733.

Table Selection of diffracting crystals

Crystal (diffracting plane)	Usual abbreviation	2d (nm)	Useful wavelength range (nm)
Lithium fluoride (420)	—	0.198	0.049—0.190
Topaz	—	0.271	0.680—0.260
Lithium fluoride (220)	—	0.285	0.071—0.274
Lithium fluoride (200)	—	0.403	0.101—0.387
Sodium chloride (200)	NaCl	0.564	0.141—0.541
Silicon (111)	Si	0.626	0.156—0.601
Germanium (111)	Ge	0.655	0.164—0.629
Pentaerythritol	P.E.T.	0.873	0.218—0.838
Ethylene diamine tartrate	EDDT	0.881	0.220—0.846
Ammonium dihydrogen phosphate	ADP	1.065	0.267—1.022
Sorbitol hexa-acetate (110)	SHA	1.398	0.350—1.342
Gypsum	—	1.515	0.379—1.454
Mica	—	1.97—1.99	0.49 —1.9
Rubidium acid phthalate	RbAP	2.621	0.629—2.516
Potassium acid phthalate	KAP	2.664	0.666—2.557
Chlinoclore	—	2.84	0.71 —2.73
Octadecyl hydrogen maleate	OHM	6.35	1.59 —6.09
Lead myristate*	—	7.90	1.98 —7.58
Diocadecyl adipate	OAO	9.38	2.35 —9.00
Lead stearate*	—	10.06	2.50 —9.66
Lead lignocerate*	—	13.0	3.25 —12.5
Lead melissate*	—	16.0	4.0 —15.4

* 'Soap films' a few tens of nm thick mounted on glass

Bibliography

The review has been written to serve as a simple introduction to *X*-ray emission spectroscopy, and to emphasise the chemical potential of the method. The list of references is not intended to be anything other than a brief selection of relevant papers. For general background reading references 3 and 9 should be consulted, but for a more detailed account of chemical effects in *X*-ray emission spectroscopy and for more comprehensive literature surveys, the following articles will be invaluable.

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D. H. Tombouliau, 'The Experimental Methods of Soft *X*-Ray Spectroscopy and the Valence Bond Spectra of the Light Elements', *Handbuch der Physik*, 1957, 30, 246, Springer-Verlag, Berlin.

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W. L. Baun, 'Instrumentation Spectral Characteristics and Applications of Soft X-Ray Spectroscopy', *Appl. Spect. Rev.*, 1968, **1**, 397.

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and A. F. Burr, 'Re-evaluation of X-Ray Atomic Energy Levels', *Rev. Mod. Phys.*, 1967, **39**, 125.