<u>Lecture 25</u> Title : X- Ray Spectra

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In this lecture, we will learn about the transitions of electrons between inner shells.

Since the energy difference is high and is of the order of X-ray, this generates the characteristic X-ray.

The X-ray fluorescence is very reach in information about the element.

In the following, we will elaborate this processes.

X rays – 100 pm, have much higher frequencies than visible light rays.

X-ray spectrum involves the deeper energy levels of heavy atoms.

Energy of electron-nuclear interaction is clearly dominant compared with the energies corresponding to other interactions.

Absorption spectra of X- rays:

X- rays can pass through matter but their intensity is reduced while doing so.

Attenuation depends on the material though which they pass. It also depends on the frequencies.

High frequency X-ray (energy $h\nu$ > 100 *Kev* or short wavelength) -hard X rays – attenuated less than soft X rays $\lambda \leq$ 10pm low frequency X rays (energy $h\nu \geq 1$ *Kev* or long wavelength $\lambda \geq 1$ *nm*). This attenuation is not a monotonic function of frequency.

Figure 25.1 shows the block diagram of the absorption experimental set up.

X ray source: emits radiation having a continuous distribution over a very wide frequency range.

Crystal spectrometer: Serves as a monochromator, receives all the radiation but only lets through monochromatic radiation of a particular frequency ν .[($2d \sin\theta = {}^{kc}\!/_{\nu}$)]

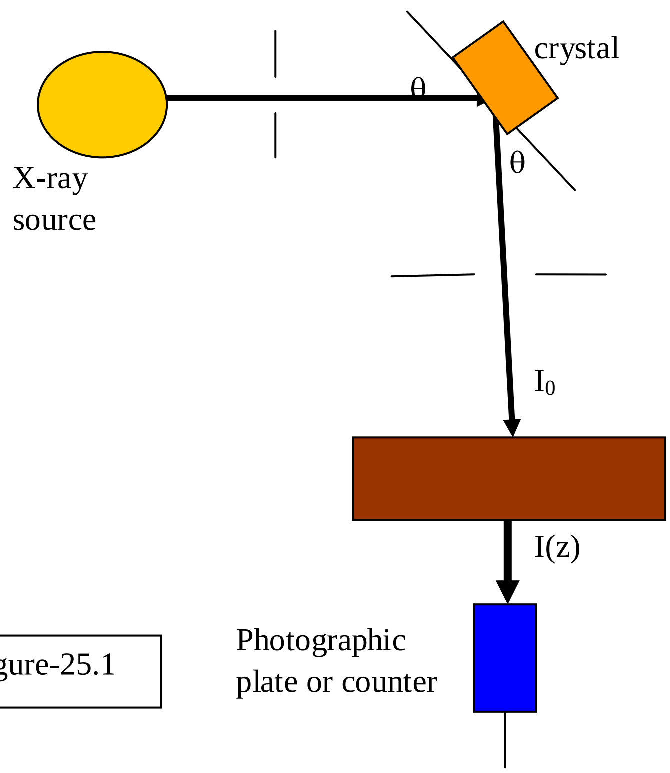


Figure-25.1

I (z) is the intensity after absorption. It can be shown that

$$\frac{dI}{I} = -kdz \text{ or } I(z) = I_0 e^{-kz} \quad \text{..................................(25.1)}$$

Absorption coefficient k depends on frequency and the characteristics of the absorbing material.

Changing the angle of the crystal spectrometer $\rightarrow$ vary radiation frequency $\rightarrow$ get the curve k as a function of the frequency. The absorption spectrum is as shown in figure-25.2.

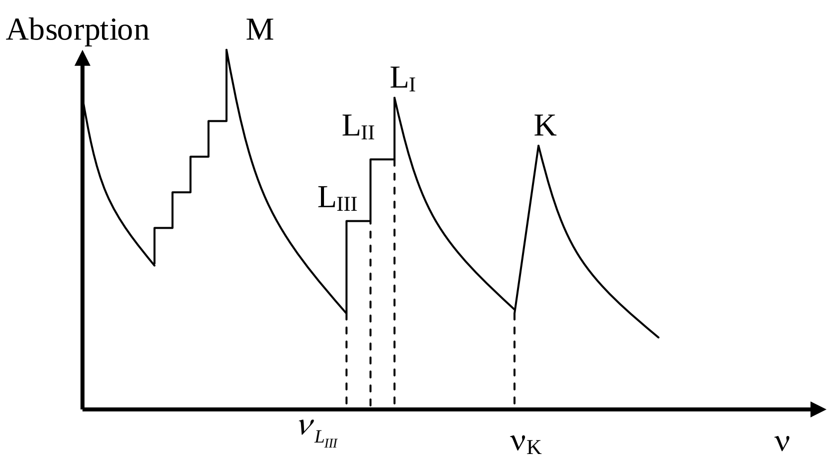


Figure-25.2

The smooth parts vary as, $\frac{c}{\nu^3}$.

A discontinuity, called K discontinuity is observed at much higher frequency.

As the frequency decreases three closely separated discontinuities L_I, L_{II}, L_{III} may be observed,

There five discontinuities for M and seven for N.

The frequencies at which discontinuities occur are characteristics of the chemical elements, those are to say of different types of atoms, independent of the molecules of which they form a part.

Comment:

(i) These statements are true only to a first approximation.

(ii) Each of the discontinuities is composed of several closely spaced discontinuities.

(iii) Very small frequency shift is observed according to the molecules in which the element occurs.

Explanations:

X- Rays may be absorbed by many simultaneous processes acting in competition and the measured absorption coefficient K can then be considered as the sum of partial coefficients that would correspond to each of the processes acting in isolation. Each of the frequency discontinuities behaves as a threshold above which a new process contributes to the absorption; this particular process cannot occur when the frequency is below the threshold.

$$h\nu \geq h\nu_k$$

This phenomenon is same as photo electric effect. $h\nu_k \geq w_s = h\nu_s$ Binding energy is

$$E_k \geq -h\nu_k$$

Thus each of the absorption discontinuities may be interpreted as a photoelectric threshold; each of the discontinuities corresponds to a different escape energy, in other words to the detachment of the electron of different binding energy.

X-Ray emission Spectra:

A piece of metal wire called anticathode is bombarded with highly accelerated electrons. The piece of metal becomes a source of X radiation. This radiation can be analyzed with a crystal spectrometer. The observed emission spectrum is shown in figure-25.3

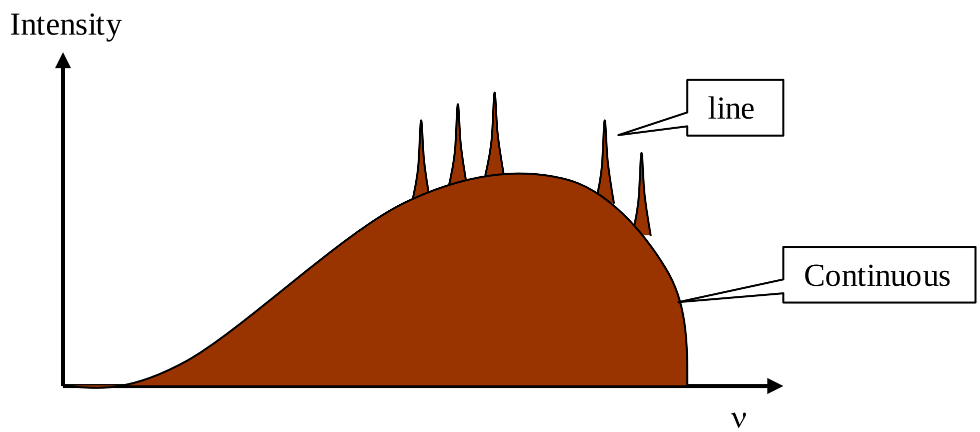


Figure – 25.3

In Figure-25.3, the emission spectrum consists of two parts:

(i) Continuous spectrum

(ii) Line spectrum.

It consists of a line spectrum with a background continuum. X - ray fluorescence producing X- radiation having only a line spectrum without a background continuous spectrum.

(i) Continuous spectrum:

Continuous spectrum depends little on the metal used for the anticathode; the height of the curve increases with the increase of the Z of the metal, but the shape of the curve is independent of z. ν_{max} is completely independent of metal used for the anticathode.

$$I(\nu) = const \times Z(\nu_{\max} - \nu)$$

The curve is strongly depending on the voltage V used for accelerating the electron. The maximum frequency increases proportionally with the voltage V.

$$eV = h\nu_{\max}$$

Since the continuous spectrum depends strongly on the velocity of the incident electron, it may be surmised that the corresponding X- radiation is emitted by these electrons.

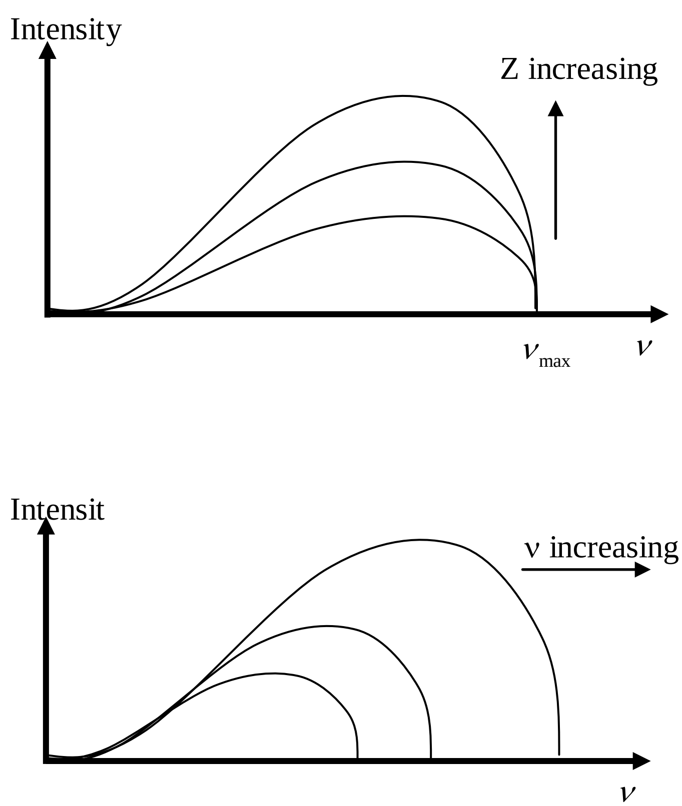


Figure-25.4

Classical explanation:

When electrons moving at high velocities reach the anti cathode, they are subjected to strong electrostatic forces arising mainly from the nuclei of the constituent atoms.

The electron is strongly accelerated and according to classical theory of radiation “the electrostatic changes emit electromagnetic waves and the greater the acceleration, the higher their frequency.

It is the sudden slowing down of the electrons when they penetrate the anticathode, which is responsible for the continuous spectrum; this may be described as deacceleration radiation but often the German term Bremsstrahlung is used.

Quantum explanation:

This problem can be treated as elastic collision between an incident electron collision between an incident electron and a stationary target nucleus, in which part of kinetic energy of the electron is transferred into kinetic energy of photon.

The energy of the projectile is much smaller than the rest energy of the target nucleus and as always the target nucleus takes up momentum but receives hardly any energy.

Maximum energy electron can provide is its entire maximum kinetic energy .so,

$$h\nu_{\max} = \frac{1}{2} m V_{electron}^{2} = eV$$

(ii) Line Spectrum:

Characteristics:

(i) Line spectrum depends mainly on the material from which the X –rays originates, either the anticathode of the X – ray tube or absorbing material used in a fluorescence experiment.

(ii) The frequencies of the spectral lines are independent of the voltage which accelerates the electrons and independent of the frequency of the incident radiation. Depends only on the chemical elements of which the material is composed.

(iii) The frequencies are characteristics of the atoms of the chemical elements.

Comparison with optical spectra:

(a) The lines are grouped in series, appearing in distinct regions of frequency.

(b) The lines obey the Ritz combination principle;

$$\frac{1}{\lambda_{np}} = \frac{v_{np}}{c} = T_p - T_n$$

Or, in other word they can also be interpreted as transitions between energy levels of that element.

In the following figure – 25.5, the absorption and emission at different accelerated potential are plotted on the same graph.

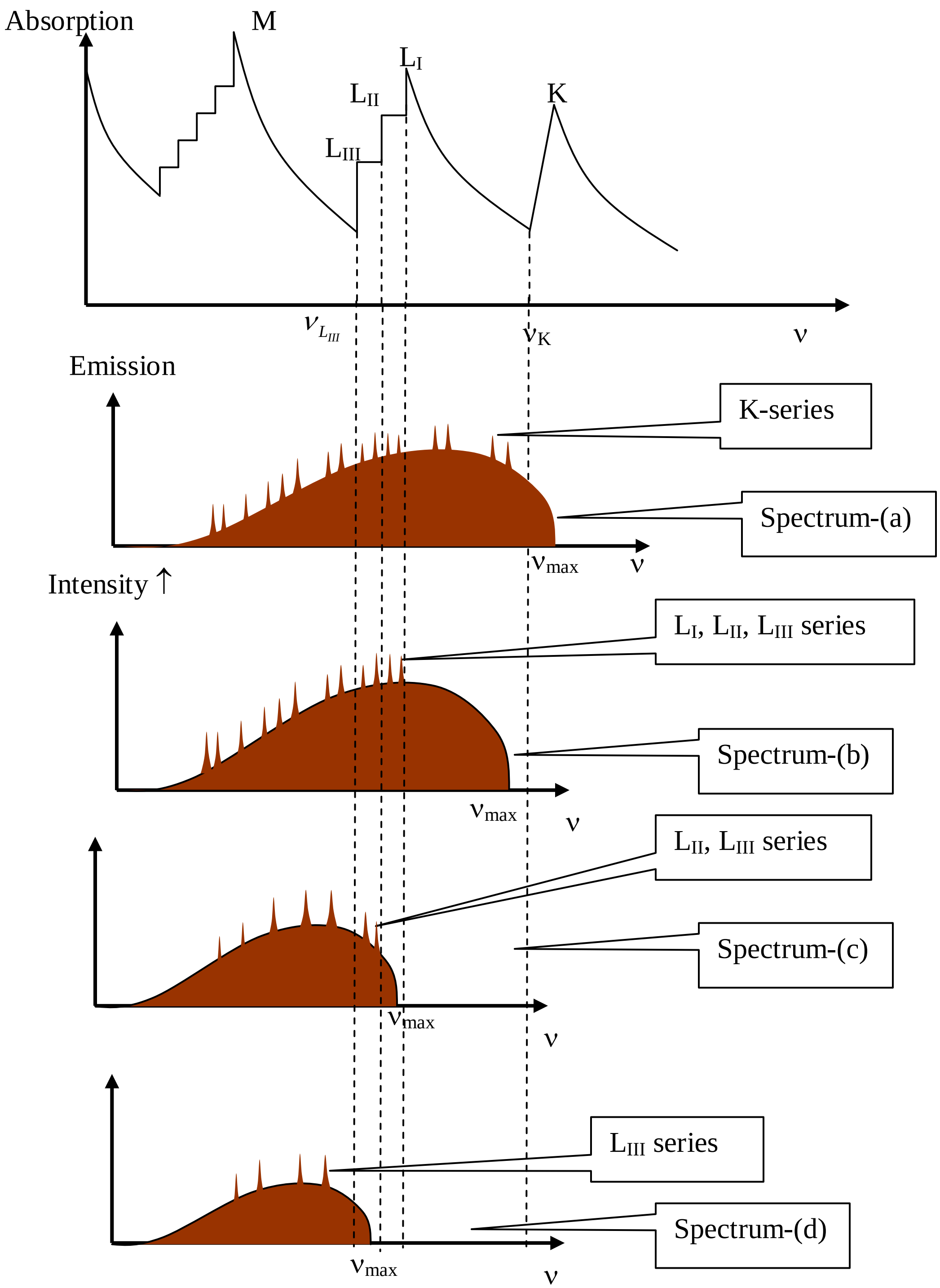


Figure -25.5

Conditions for observing X-rays:

(1) The maximum frequency ν_{max} of the continuous spectrum is greater than the frequency of the corresponding absorption discontinuity.

$$v_{\max} > v_k \quad or \quad v_L, v_M$$

$$\frac{1}{2}mV^2 = eV = hv_{\max} > hv_k = w_k$$

(2) If $ev \geq hv_{L1}$, the three series L_1, L_{11} & L_{111} are observed. Similarly the other series also.

All this may be explained by making the hypothesis that the number of places available for the electrons in each energy level is limited.

The emission of X –ray photons by an atom occurs by spontaneous rearrangement of its electrons, following the creation of an empty space in one of its deeper energy levels by ionization.

(3) A complete series appears in the spectrum on condition that the frequency v of the primary radiation is greater than the frequency of the corresponding absorption discontinuity.

The following table includes some X-ray transitions of K and L series.

		Upper energy levels of transitions											
Series	L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V	N_I	N_{II}	N_{III}	N_{IV}	N_V....
K		K_{α_2}	K_{α_1}		K_{β_2}	K_{β_1}				K_{γ_2}	K_{γ_1}		
L_I					L_{β_4}	L_{β_3}				L_{γ_2}	L_{γ_3}		
L_{II}				L_η			L_{β_1}		L_{γ_5}			L_{γ_1}	
L_{II}				L_l			L_{α_2}	L_{α_1}	L_{β_6}			$L_{\beta_2'}$	L_{β_2}

The concept of these transitions will be clear from the figure-25.6.

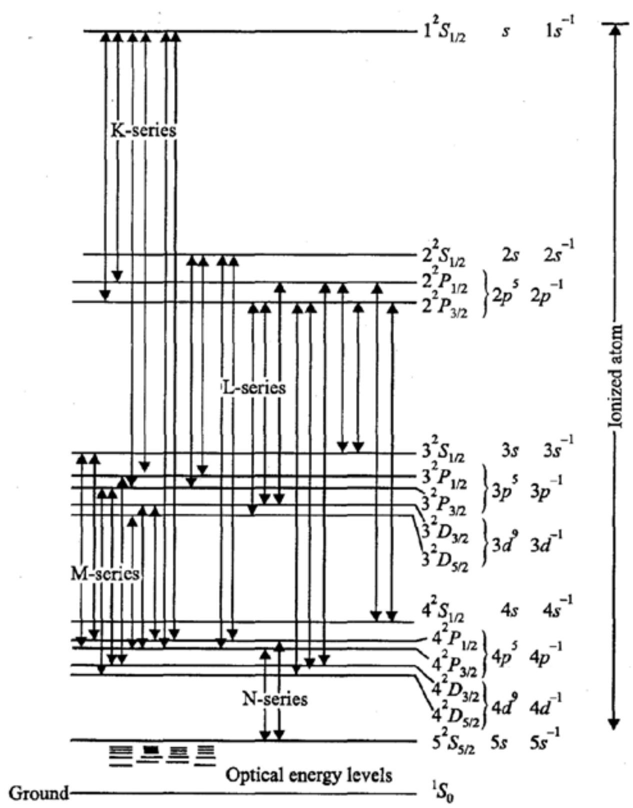
The energy levels are drawn in the following manner.

(a) The ground state is the one where all the electrons are intact.

(b) The highest energy state is obtained by removing one electron from the 1s orbital and represented as $1s^{-1}$.

(c) Similarly the $2p^{-1}$ represents that there is a vacancy in 2p orbital and it gives rise to ${}^2P_{1/2}$ and ${}^2P_{3/2}$ levels.

(d) The vertical arrows show the possible transitions with the selection rule $\Delta L = \pm 1$ and $\Delta J = 0, \pm 1$.



X-ray energy levels of Cd

Figure-25.6

So, what we learnt that X-ray spectra include a limited number of lines which can be grouped into a few series. These series are designated as K, L, M, and N…….

To a good approximation, the first line of the K series K_α, can be described for atoms with different nuclear charge number Z by the expressions.

$$\overline{v_{k\alpha}} = R(Z-1)^2(\frac{1}{1^2}-\frac{1}{2^2}) = \frac{3}{4}R(Z-1)^2$$

The first line of the L series.

$$\overline{v_{L\alpha}} = R(Z-7.4)^2(\frac{1}{2^2}-\frac{1}{3^2}) = \frac{5}{36}R(Z-7.4)^2$$

And the energy

$$\begin{aligned} &E_n = -Rhc\frac{(Z-s_n)^2}{n^2} \\ &K \quad s_1 = 1 \; to \; 2 \\ &L \quad s_2 \approx 10 \\ &M \quad s_3 \approx 20 \end{aligned}$$

Linear relationship should expect by plotting $\sqrt{\nu}$ vs Z for different elements. This is known as Moseley's law.

Figure-25.7 show the Mosley diagram of X-ray absorption edges.

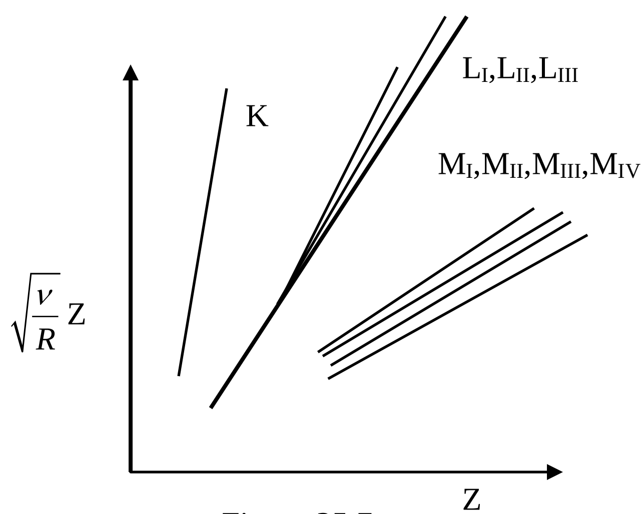


Figure-25.7

The Auger effect:

Not all atoms from which electrons have been removed from inner shells by electron bombardment or other forms of energy transfer return to the ground state by emitting X-rays. Observed quantum yield is less than 1.

$$\eta = \frac{Number\ of\ X - ray\ emitting\ atoms}{Number\ of\ K, L, ...ionised\ atoms.}$$

Thus it must be possible for the atoms to return to ground state without emitting radiation. The probability of such non-radiative process, which complete with X-ray emission, has been found to decrease with increasing nuclear charge.

The non-radiative return to ground states accomplished by auger effect. L shell loses two electros. These are then replaced by electrons from shells further out, M shell and so on. The K.E. of auger electron, $E_{kin} = h\nu_{k\alpha} - E_L = E_k - E_L - E_L = E_k - 2E_L$

Example: Silver is bombarded with K_α radiation from tungsten (energy = 59.1 keV). Electrons with 55.8 kev, 33.8 kev, 21.3 kev, 18.6 kev are observed. (Z = 47)

$E_k = 25.4 KeV, E_L = 3.34 KeV, E_{k\alpha} = 22.1 KeV, E_{k\beta} = 24.9 KeV$

(1) 55.8 Kev $\quad E_{ion\,L} = 3.34\,KeV$, $So,\ 59.1 - 3.34 = 55.76 KeV$ Photoelectrons from L shell.

(2) 33.8 Kev $\quad E_{ion\,k} = 25.4\,KeV$, $So,\ 59.1 - 25.4 = 33.7 KeV$ Photoelectrons from k shell.

(3) 21.3 Kev $\quad E_{k\beta}(Ag) = 24.9 KeV$, $So,\ E_{k\beta}(Ag) - E_{ion\,L} = 24.9 - 3.34 = 21.56 KeV$ Auger electrons

(4) 18.6 Kev $\quad E_{k\beta}(Ag) = 22.1 KeV$, $So,\ E_{k\alpha}(Ag) - E_{ion\,L} = 22.1 - 3.34 = 18.76 KeV$ Auger electrons

Recap

In this lecture we learnt the process of generating X-rays. This is the transitions within the inner shells. The X-ray spectrum consists of line and continuum spectra.

The continuum spectrum does not depend on the element but depends on the accelerating voltage.

Line spectrum is the characteristics of the element.

There are several applications of X-rays. However, these line spectrum provides to develop Photoelectron spectroscopy (XPS), Electron spectroscopy for chemical analysis (ESCA)

In this, sample is irradiated with characteristic X ray.

Kinetic Energy = irradiant photon- binding energy.

This gives information about the binding energy of inner electron with atoms. It helps to carry out chemical compositions of the sample.