

# 8

## X-Ray Spectroscopy\*

### 8.1. ORIGIN OF X-RAY SPECTRA

X-rays were discovered in 1895 by Wilhelm Conrad Röntgen who received the first Nobel Prize in Physics, awarded in 1901, for his discovery. X-ray absorption, emission, and fluorescence spectra are used in the qualitative and quantitative determination of elements in solid and liquid samples. X-ray absorption is used in the nondestructive evaluation of flaws in objects, including voids or internal cracks in metals, cavities in teeth, and broken bones in humans, a technique called radiography or X-ray fluoroscopy. This same technique is used to perform security screening of baggage at airports. A computerized version of radiography, computed tomography (CT) scanning or computed axial tomography (CAT) scanning, provides a powerful, high-resolution medical diagnostic tool by giving a 3D cross-sectional image of body tissues. Diffraction of X-rays by crystalline materials, a technique called X-ray crystallography, provides crystal structure identification, orientation of atomic planes in materials, and other physical information about samples. X-ray astronomy uses cosmic X-rays to study the universe and X-ray spectrometers have been sent to the moon and Mars to study the surface rocks *in situ*. This chapter will focus on X-ray fluorescence spectrometry (XRF) and X-ray diffractometry (XRD), the techniques of most use to analytical chemists.

X-rays consist of electromagnetic radiation with a wavelength range from 0.005 to 10 nm (0.05–100 Å). X-rays have shorter wavelengths and higher energy than UV radiation. X-rays are generated in several ways, such as when a high-speed electron is stopped by a solid object or by electronic transitions of inner core electrons.

#### 8.1.1. Energy Levels in Atoms

An atom is composed of a nucleus and electrons. The electrons are arranged in shells around the nucleus with the valence electrons in the outer shell. The different shells correspond to the different principal quantum numbers of the possible quantum states. The principal quantum number,  $n$ , can have integral values beginning with 1. The shells are named starting with the shell closest to the nucleus, which is called the K shell. The K shell is the lowest in energy and corresponds to the quantum level with  $n = 1$ . The shells moving out from the nucleus are named the L shell, M shell, and so on alphabetically. The letters used for the two lowest shells are historical; K is from the German word

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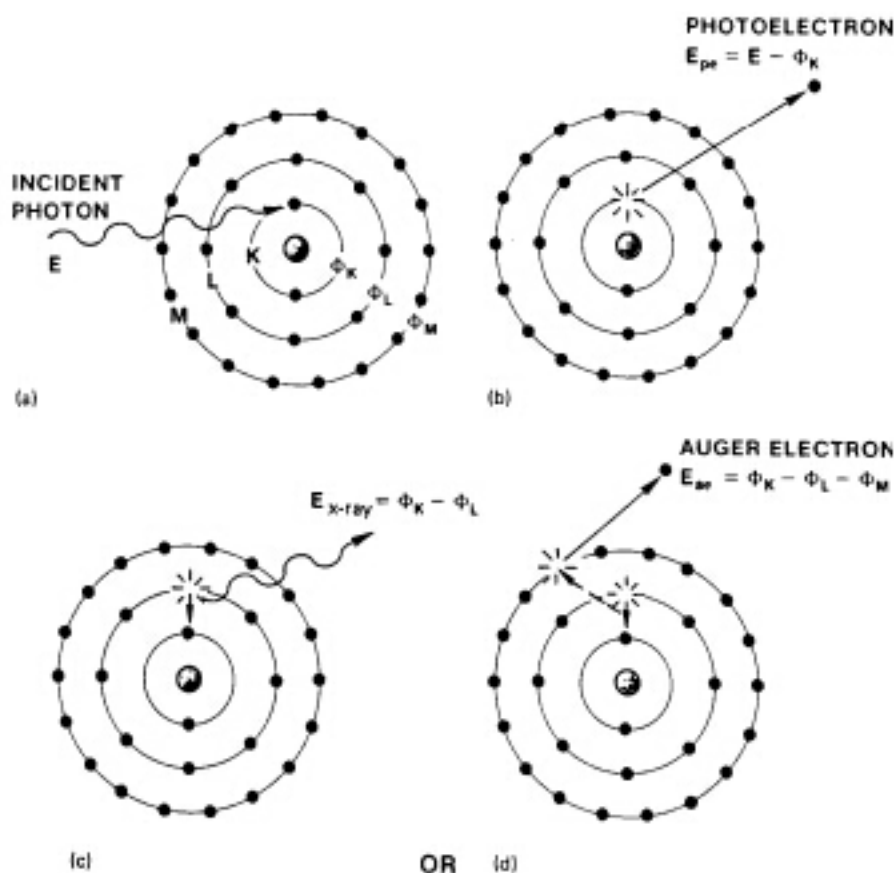
\*Dedicated to the memory of Dr. Ron Jenkins, an outstanding X-ray spectroscopist, teacher, and mentor.

*kurz*, meaning short, L is from the German word *lang*, meaning long. An atom is shown schematically in Fig. 8.1(a), with  $\Phi_K$ ,  $\Phi_L$ , and  $\Phi_M$  representing the energy of the K, L, and M shells, respectively. A partial list of elements and their electron configurations is given in Table 8.1. For example, a sodium atom contains filled K and L shells and one electron in the M shell.

When an X-ray or a fast-moving electron collides with an atom, its energy may be absorbed by the atom. If the X-ray or electron has sufficient energy, it knocks an electron out of one of the atom's inner shells (e.g., the K shell) and the atom becomes ionized as shown in Fig. 8.1(b). An electron from a higher-energy shell (e.g., the L-shell) then falls into the position vacated by the dislodged inner electron and an X-ray photon is emitted as the electron drops from one energy level to the other [Fig. 8.1(c)]. The wavelength of this emitted X-ray is characteristic of the element being bombarded.

A fourth process can also occur, as shown in Fig. 8.1(d). Instead of emitting an X-ray photon, the energy released knocks an electron out of the M shell. This electron is called an Auger electron. This Auger process is the basis for a sensitive surface analysis technique. Auger electron spectroscopy and the related method of X-ray photoelectron spectroscopy, based on the measurement of the emitted electron shown in Fig. 8.1(b), are discussed in Chapter 14.

If we plot the energy levels of the K, L, and M shells for a given element, we get a diagram similar to Fig. 8.2. Note that the K shell has only one energy level, while the



**Figure 8.1** A schematic atom showing the steps leading to the emission of an X-ray photon (c) or an Auger electron (d). (From Jenkins et al., 1981, used with permission.)

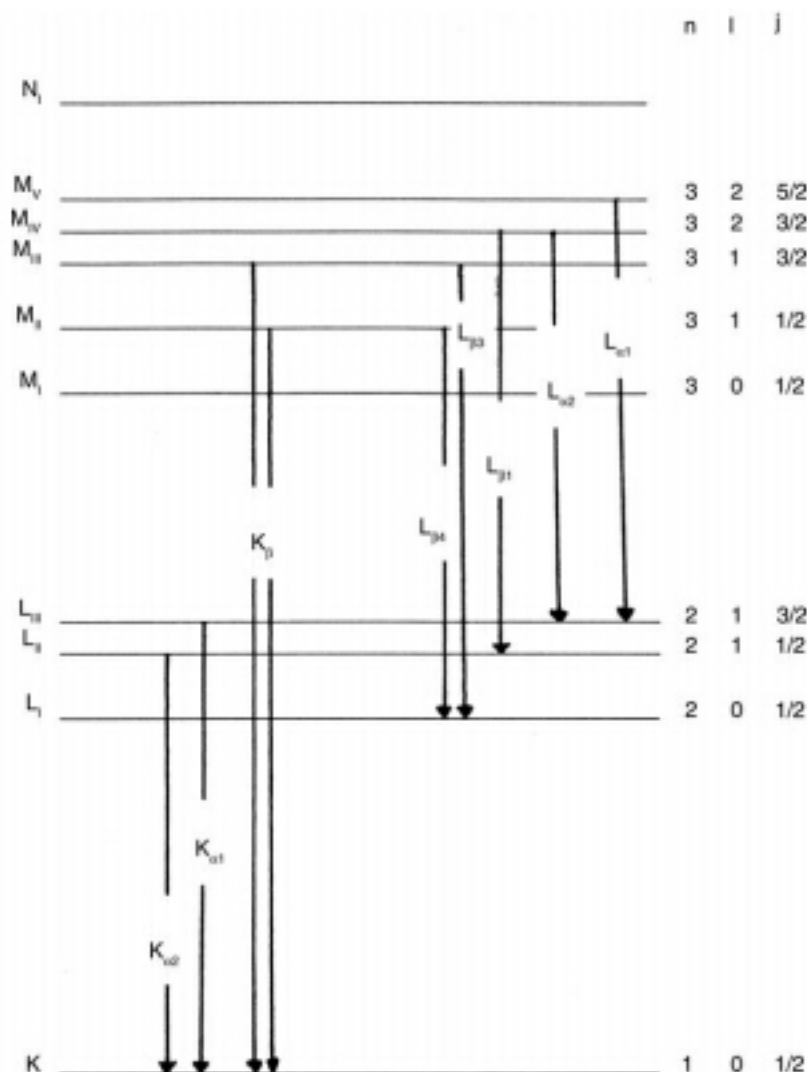
**Table 8.1** Electron Configurations of Various Elements

Element	Z	K			L			M			N	
		1s	2s	2p	3s	3p	3d	4s	4p			
H	1	1										
He	2	2										
Li	3	2	1									
Be	4	2	2									
B	5	2	2	1								
C	6	2	2	2								
N	7	2	2	3								
O	8	2	2	4								
F	9	2	2	5								
Ne	10	2	2	6								
Na	11	Neon core (10)			1							
Mg	12				2							
Al	13				2	1						
Si	14				2	2						
P	15				2	3						
S	16				2	4						
Cl	17				2	5						
Ar	18				2	6						
K	19		Argon core (18)								1	
Ca	20										2	
Sc	21								1		2	
Ti	22								2		2	
V	23								3		2	
Cr	24								5		1	
Mn	25								5		2	
Fe	26								6		2	
Co	27								7		2	
Ni	28								8		2	
Cu	29								10		1	
Zn	30		Cu <sup>+</sup> core (28)								2	
Ga	31										2	1
Ge	32										2	2
As	33										2	3
Se	34										2	4
Br	35										2	5
Kr	36										2	6

higher shells have sublevels within each shell. If an electron is dislodged from the K shell, an electron from an L or an M shell may replace it. The resulting ion emits radiation with energy  $E$  equal to the energy difference between the electronic energy levels, such as:

$$E_{X\text{-ray}} = \Phi_L - \Phi_K \quad (8.1)$$

where  $\Phi_L$  is the energy of the electron in a specific electronic state within the L shell that "drops" to the K shell. Similar equations may be written for other transitions, such as between an M shell sublevel and an L shell sublevel, using the appropriate energy of the electron in the M shell sublevel that drops into the L shell and so on. As we know



**Figure 8.2** Atomic energy levels and symbols used for some common X-ray transitions. (Modified from Parsons, 1997, used with permission.)

from Chapter 2,

$$E = h\nu = hc/\lambda$$

Therefore, for the X-ray photon released when an L electron in a specific sublevel drops down to fill a vacancy in the K shell,

$$h\nu = hc/\lambda = \Phi_L - \Phi_K$$

Hence the frequency of the emitted X-ray is

$$\nu = \frac{\Phi_L - \Phi_K}{h} \quad (8.2)$$

The frequency or wavelength for transitions between other sublevels and shells is calculated in the same manner. Transitions are not possible between all available energy levels.

As in all forms of spectroscopy, transitions are governed by quantum mechanical *selection rules*. Some transitions are allowed by these rules while others are forbidden. For a brief discussion of the selection rules, the interested student should consult the texts by Jenkins or Bertin listed in the bibliography.

X-ray emission lines from electron transitions terminating in the K shell are called K lines, lines from transitions terminating in the L shell are called L lines, and so on. There are three L levels differing by a small amount of energy and five M levels. These sublevels are different quantum states, as shown in Fig. 8.2; the quantum numbers and states will not be discussed in detail. An electron that drops from an L shell sublevel to the K shell emits a photon with the energy difference between these quantum states. This transition results in a  $K_{\alpha}$  line. There are two possible  $K_{\alpha}$  lines for atoms with atomic number  $> 9$ :  $K_{\alpha 1}$  and  $K_{\alpha 2}$ , which originate in different sublevels of the L shell. The  $K_{\alpha}$  lines are often not resolved, and only one peak is seen. These lines are illustrated in Fig. 8.2. The use of a Greek letter and numerical subscript to identify an X-ray emission line is called the *Siegbahn* notation. For the purposes of this text, the notation is just a "name" for the peak. An electron that drops from an M shell sublevel to the K shell generates a  $K_{\beta}$  X-ray. There is more than one  $K_{\beta}$  line, but the energy differences are so small between  $K_{\beta 1}$  and  $K_{\beta 2}$  that only a single  $K_{\beta}$  line is seen unless a high-resolution spectrometer is used. If an electron is ejected from an L shell, an electron from an M shell may fall into its place and emit an X-ray of characteristic wavelength with energy equivalent to the difference between the L and M shell sublevels. These are designated as L lines. A number of L lines are possible, as indicated by Fig. 8.2. Table 8.2 indicates the actual transition that gives rise to selected X-ray emission lines. Electrons originating in an N or O shell and falling into the L shell also generate L lines. The energy levels of the K, L, M, and higher shells are characteristic of the element being examined and the sharp emission lines resulting from electronic transitions are called *characteristic lines* or characteristic radiation. A schematic X-ray emission spectrum obtained under certain conditions by bombarding a solid metal, such as rhodium or lead or tungsten, with high-energy electrons is shown in Fig. 8.3. The characteristic lines are shown as sharp peaks on a broad continuous background. The characteristic K X-ray emission lines from some elements are given in Table 8.3. A more comprehensive table of K and L lines for the elements is found in Appendix 8.1 and in handbooks such as the CRC Handbook of Chemistry and Physics and the CRC Handbook

**Table 8.2** Electron Transitions for Selected X-Ray Emission Lines

Siegbahn line designation	Electron transition	Siegbahn line designation	Electron transition
$K_{\alpha 1}$	$L_{III} \rightarrow K$	$L_{\beta 1}$	$M_{IV} \rightarrow L_{II}$
$K_{\alpha 2}$	$L_{II} \rightarrow K$	$L_{\beta 2}$	$M_{III} \rightarrow L_{I}$
$K_{\beta 1}$	$M_{III} \rightarrow K$	$L_{\beta 3}$	$M_{II} \rightarrow L_{I}$
$K_{\beta 2}$	$M_{II} \rightarrow K$	$L_{\gamma}$	$M_{I} \rightarrow L_{II}$
$K_{\beta 3}$	$M_{IV, V} \rightarrow K$	$L_{\gamma 2}$	$N_{II, III} \rightarrow L_{I}$
$K_{\beta 4}$	$N_{II, III} \rightarrow K$	$L_{\beta 4}$	$N_{I} \rightarrow L_{III}$
$K_{\beta 5}$	$N_{IV, V} \rightarrow K$	$M_{\zeta 1}$	$N_{III} \rightarrow M_{V}$
$L_{\alpha 1}$	$M_{IV} \rightarrow L_{III}$	$M_{\zeta 2}$	$N_{II} \rightarrow M_{IV}$
$L_{\alpha 2}$	$M_{IV} \rightarrow L_{III}$		

*Note:* Not all lines are seen for all elements, and many of the lines are not resolved with standard X-ray spectrometers. Many  $M \rightarrow M$ ,  $N \rightarrow M$ ,  $O \rightarrow L$ , and  $O \rightarrow M$  transitions have no Siegbahn notation associated with them.