

10.3.4.8 X-ray spectroscopy

10.3.4.8.1 Introduction

This section presents a new notation for X-ray emission lines and absorption edges to be called the *IUPAC Notation* to replace the existing Siegbahn nomenclature by a system based upon the energy-level designation. This IUPAC X-ray nomenclature has the advantage of being simple and easy to extend to any kind of transitions. It is consistent with the notation used in electron spectroscopy and is closely related to that of Auger electron spectroscopy. Units and conversion factors for X-ray wavelengths and energies are also given. (See also the corresponding sections of Chapter 17.)

10.3.4.8.2 Terms currently used to describe X-ray spectra

X-ray radiation may result from the interaction of high energy particles or photons with matter. *Bremsstrahlung* is the name given to the radiation emitted as a result of the retardation of high-energy particles by matter. *Synchrotron radiation* results from the acceleration of charged particles in circular orbits by strong electric and magnetic fields. Bremsstrahlung and synchrotron radiation are used in X-ray spectroscopy as sources of *continuous X-ray radiation*.

Characteristic X-ray emission originates from the radiative decay of electronically highly excited states of matter. Excitation may be by electrons, often called *primary excitation*, by photons, called *secondary* or *fluorescence excitation*, or by heavier particles such as protons, deuterons, or heavy atoms in varying degrees of ionization. The emission in the latter case is called *particle-induced X-ray emission*, (*PIXE*).

Alternatively, electronically highly excited states may decay by *radiationless transitions* leading to the ejection of additional electrons. Specific types of radiationless transitions are known as *Auger-* and *Coster-Kronig transitions*. The *fluorescence yield* is the probability that the decay of the excited state takes place with the emission of a photon.

The electronic states occurring as initial and final states of a process involving the absorption or emission of X-ray radiation are called *X-ray levels*. This term is used here with the same meaning as in the description of many-electronic states in atomic spectroscopy, i.e., as part of the conceptual hierarchy, *configuration*, *term* and *level*. It represents a many-electron state which, in the purely atomic case, has total angular momentum ($J=L+S$) as a well defined quantum number. The word 'term' in atomic spectroscopy denotes a set of levels which have the same electron configuration and the same value of the quantum numbers for total spin S and total orbital angular momentum L .

Normal X-ray levels or *diagram levels* are described by the removal of one electron from the configuration of the neutral ground state. These levels form a spectrum similar to that of a one-electron or hydrogen-like atom but, being single-vacancy levels, have the

energy-scale reversed relative to that of single-electron levels. Diagram levels may be divided into *valence levels* and *core levels* according to the nature of the electron vacancy.

Diagram levels with orbital angular momentum different from zero occur in pairs and form *spin doublets*. In the nomenclature of atomic spectroscopy they belong both to the same configuration and the same term.

X-ray levels have various degrees of ionization - single, double or higher - and may in some cases also be electrically neutral. An *excitation level*, also called an *exciton*, is an electrically neutral X-ray level with an expelled electron bound in the field of a core electron vacancy. Such levels may give rise to the *Rydberg series*.

Multiply ionized and excited levels may be produced by many-electron processes often called *electron relaxation processes* and which leads to *electron shake-off* or secondary ionization. *Electron relaxation* also produces *electron shake-up*, i.e. states with a core hole and excited valence-electron configuration. Other mechanisms leading to multiply ionized states include Auger and Coster-Kronig transitions. In collisions with heavy particles as in PIXE, multiply ionized states often dominate over the singly ionized diagram states.

The energy of X-ray levels of atoms and molecules in the gas phase is usually given relative to that of the neutral ground state; for solids it is usually given relative to the *Fermi level*. In the latter case, level energies are often referred to as *electron binding energies*. The problem of defining the reference level in insulating solids is non-trivial.

X-ray emission and absorption follow the *selection rules* for emission and absorption of electromagnetic radiation. These are the *electric dipole selection rules* leading to most intense lines, and the *magnetic dipole-* and the *electric quadrupole selection rules* attributed to certain weak features in X-ray emission spectra. Lines forbidden according to the electric dipole selection rules are sometimes called *multipole lines* or forbidden lines. The use of the latter term is discouraged.

An X-ray absorption spectrum observed at low resolution consists of one or several *absorption continua* terminated at their low energy by *absorption edges* or *absorption limits* below which the *photo-absorption coefficient* is significantly lower. The absorption limit represents the minimum energy required to excite an electron from a given one-electron state.

The position of absorption limits and continua relative to the X-ray emission spectrum is of importance for analytical applications of X-ray spectroscopy due to the process of *self-absorption*. Maxima in the absorption spectrum may be due to the presence of excitation levels as mentioned above. They may also be caused by *shape resonances* or by *many-electron* interaction resulting from electron-relaxation or "shake" effects. Structure in X-ray absorption spectra remote from the edge and extending to higher energies is called *extended X-ray absorption fine structure*, (*EXAFS*). It is due mainly to the scattering of

the expelled electron by neighbouring atoms and is not covered by the present nomenclature. Structure closer to the absorption edge is sometimes called *near-edge X-ray absorption fine structure*, (*NEXAFS*).

The characteristic X-ray emission consists of series of *X-ray spectral lines* with discrete frequencies, characteristic of the emitting atom. Other features are *emission bands* from transitions to valence levels. In a spectrum obtained with electron or photon excitation the most intense lines are called *diagram lines* or *normal X-ray lines*. They are dipole-allowed transitions between normal X-ray diagram levels.

The radiative decay of an excitation level may proceed to the neutral ground state and would thus occur at the same energy as the corresponding line in the absorption spectrum. Such a line is called a *resonance line* and the process is called *resonance emission*.

An *X-ray satellite* line is a weak line in the same energy region as a normal X-ray line. Another name used for weak features is *non-diagram line*. Recommendations as to the use of these two terms have conflicted. With the term diagram line defined as above the term non-diagram line may well be used for all lines with a different origin. The majority of these lines originate from the dipole-allowed de-excitation of multiply ionized or excited states, and are called *multiple-ionization satellites*. A line where the initial state has two vacancies in the same shell, notably the k-shell, is called a *hypersatellite*. Other mechanisms leading to weak spectral features in X-ray emission are, e.g., resonance emission, the *radiative Auger effect*, magnetic dipole and electric quadrupole transitions and, in metals, *plasmon excitation*.

Atoms with open electron shells, i.e. transition metals, lanthanides, and actinides, show a splitting of certain X-ray lines due to the electron interaction involving this open shell. Structures originating in all these ways as well as structures in the valence band of molecules and solid chemical compounds have in the past been given satellite designations. In PIXE multiple-ionization lines often have greater intensity than diagram lines. In such a case the designation of the former as satellites is obviously out of place. The multitude of mechanisms collected under the term satellite and the intensity ambiguities observed in PIXE make the unqualified use of the satellite concept meaningless except as a temporary measure. If the origin of a weak line or structure is known, it should be named after that origin and not as a satellite.

10.3.4.8.3 Principles of the IUPAC notation

X-ray levels are defined as those states which occur as initial and/or final states in X-ray transitions. *Diagram levels* are those which can be described by the removal of one electron from a closed-shell electron configuration. Table 10.10 shows the relation between X-ray diagram levels and electron configurations. Note that the level notation is used for many electron systems with vacancies, not for the electrons removed from these systems. This usage conforms with common principles of spectroscopy but differs from

that of, e.g., solid-state physics, which uses a *one-electron description* with the energy level ordering reversed relative to that of spectroscopic conventions. Fig. 10.13A shows schematically the ordering of X-ray levels. Fig. 10.13B shows the ordering of one-electron levels. It is recommended that one-electron levels are denoted by the orbital notation (1s, 2s, 2p₋ etc.). The importance of separating the two kinds of notation will be further exemplified below (compare also L.G. Parratt, Rev. Mod. Phys. 31, 616 (1959)).

TABLE 10.10 Correspondence between X-ray diagram levels and electron configuration

Level	Electron configuration	Level	Electron configuration	Level	Electron configuration
K	1s ⁻¹	N ₁	4s ⁻¹	O ₁	5s ⁻¹
L ₁	2s ⁻¹	N ₂	4p ₋ ⁻¹	O ₂	5p ₋ ⁻¹
L ₂	2p ₋ ⁻¹	N ₃	4p _{3/2} ⁻¹	O ₃	5p _{3/2} ⁻¹
L ₃	2p _{3/2} ⁻¹	N ₄	4d _{3/2} ⁻¹	O ₄	5d _{3/2} ⁻¹
M ₁	3s ⁻¹	N ₅	4d _{5/2} ⁻¹	O ₅	5d _{5/2} ⁻¹
M ₂	3p ₋ ⁻¹	N ₆	4f _{5/2} ⁻¹	O ₆	5f _{5/2} ⁻¹
M ₃	3p _{3/2} ⁻¹	N ₇	4f _{7/2} ⁻¹	O ₇	5f _{7/2} ⁻¹
M ₄	3d _{3/2} ⁻¹				
M ₅	3d _{5/2} ⁻¹				

The X-ray level notation follows earlier conventions except for a minor point. The IUPAC notation prescribes Arabic numerals for subscripts. This agrees with common usage, e.g., in Auger electron spectroscopy, but differs from the original notation which used Roman numerals (L_{II} and L_{III}, instead of L₂ and L₃). The subscripts may be dropped when they are unknown or irrelevant. When the spin-orbit interaction is unresolved one may write, e.g. L_{2,3} for a state with a 2p vacancy. The atomic description is not valid for the outermost valence electrons in molecules and solids where chemical interactions and/or solid-state effects are important. States with a valence-electron vacancy are denoted by V.

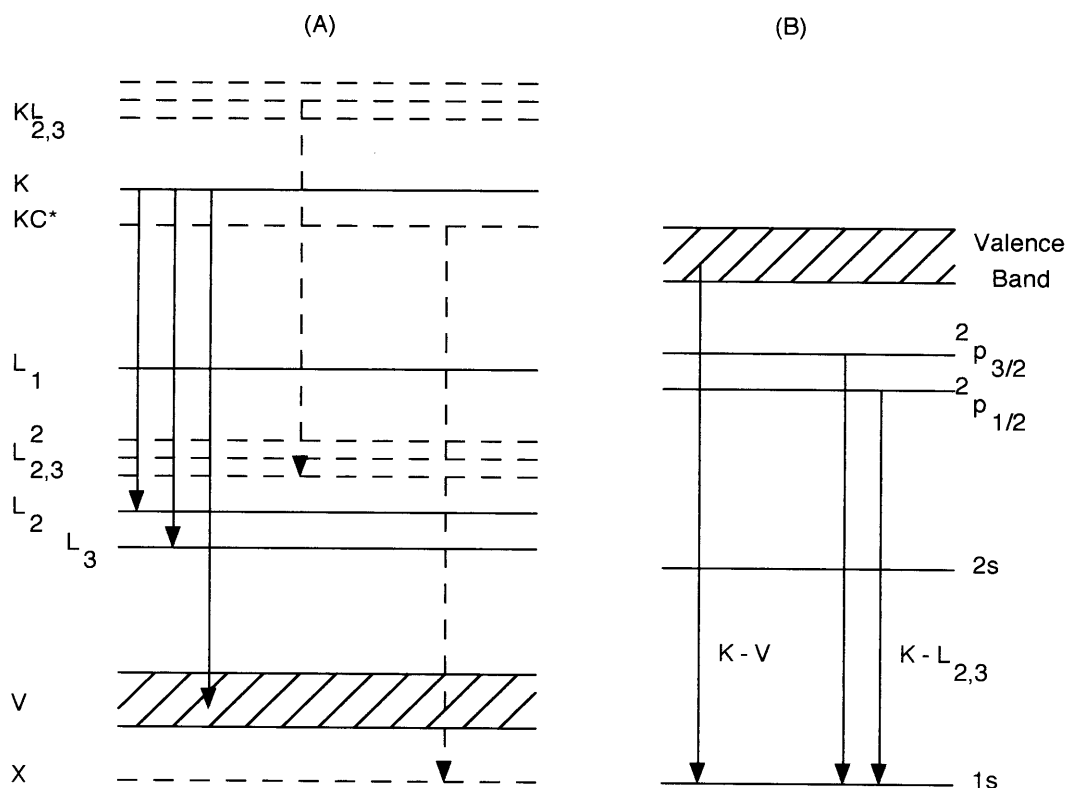


Fig.10.13 (A): Schematic X-ray level diagram. Non-diagram levels and transitions are indicated by broken lines (not to scale), (B): The corresponding one-electron energy level diagram with diagram transitions indicated

States with double or multiple vacancies should be denoted by:

$$\begin{array}{ll}
 K^2 & 1s^{-2} \\
 KL_1 & 1s^{-1} 2s^{-1} \\
 L_{2,3}^n & 2p^{-n}
 \end{array}$$

Because of electron interaction this notation does not in general give a complete description of the level structure. When desired one may therefore add the electronic term symbol of atomic or molecular spectroscopy in parenthesis after the level symbol, e.g. $KL_1(^1S)$ or $KL_1(^3S)$.

So far, the X-ray level nomenclature has not had a symbol for the neutral ground state nor for states with electrons in orbitals which are empty in the neutral ground state. The IUPAC Notation recommends the notation X for the neutral electronic ground state. This convention is close to that used for molecular electronic spectra.

There is no precedent for the notation for X-ray levels with electrons in normally empty orbitals or bands. IUPAC recommends the use of the letter C (or C*) to denote a state with an electron added in an orbital or band which is empty in the neutral ground state. In X-ray emission this letter will only occur in combinations with letters denoting vacancies, e.g., for a diatomic molecule: $KC(^1\pi)$ meaning the state with a K-shell electron promoted to an empty orbital resulting in a quasi-bound state of π symmetry. Alternatively, one may write $KC^*(^1\pi)$. The superscript * is optional and is intended to separate the neutral KC^* state from, e.g., a doubly ionized state KL_1 .

As the main rule, transitions between X-ray levels are denoted by the level symbols for initial and final state separated by a hyphen. The initial state is placed first, irrespective of the energetic ordering. As explained above the X-ray level notation conforms with a many-electron description of electronic structure. The notation for transitions will therefore frequently differ from that obtained from an "active electron" or one-electron approach. See further below.

X-ray absorption takes place from the neutral ground state to excited states with an inner vacancy. The ejected electron may go into either a bound-state or a continuum orbital. When the ejected electron is not considered the corresponding symbol is omitted.

Examples:

X-K ejected electron not considered
 X-KC or
 X-KC* ejected electron bound

In the 'active electron' picture the X-KC (X-KC*) transition might be denoted $1s \rightarrow np$. The difference between this picture and the IUPAC Notation has to be kept in mind. X-ray absorption edges can also be denoted by the word 'abs' in front of the final-state level. X-K and abs K are thus synonymous.

When possible the main rules are followed. X-ray emission diagram lines are written with the initial and final X-ray levels separated by a hyphen. The hyphen is essential in order to avoid confusion with double-hole levels. As examples we quote:

K-L₃ ($K\alpha_1$ in the Siegbahn notation) denotes the filling of a 1s hole by a $2p_{3/2}$ electron, i.e. in the "active electron" picture $2p_{3/2} \rightarrow 1s$.

K-V (for elements and compounds of Na to Cl previously denoted by $K\beta_1$, $K\beta'$, $K\beta''$ etc.) denotes the filling of a 1s hole by an electron from the valence shell.

The correspondence between Siegbahn and IUPAC Notation is given in Table 10.11.

TABLE 10.11 Correspondence between the Siegbahn and IUPAC notations

Siegbahn	IUPAC	Siegbahn	IUPAC	Siegbahn	IUPAC	Siegbahn	IUPAC
$K\alpha_1$	K-L ₃	$L\alpha_1$	L ₃ -M ₅	$L\gamma_1$	L ₂ -N ₄	$M\alpha_1$	M ₅ -N ₇
$K\alpha_2$	K-L ₂	$L\alpha_2$	L ₃ -M ₄	$L\gamma_2$	L ₁ -N ₂	$M\alpha_2$	M ₅ -N ₆
$K\beta_1$	K-M ₃	$L\beta_1$	L ₂ -M ₄	$L\gamma_3$	L ₁ -N ₃	$M\beta$	M ₄ -N ₆
$K\beta_2^I$	K-N ₃	$L\beta_2$	L ₃ -N ₅	$L\gamma_4$	L ₁ -O ₃	$M\gamma$	M ₃ -N ₅
$K\beta_2^{II}$	K-N ₂	$L\beta_3$	L ₁ -M ₃	$L\gamma_4'$	L ₁ -O ₂	$M\zeta$	M _{4,5} -N _{2,3}
$K\beta_3$	K-M ₂	$L\beta_4$	L ₁ -M ₂	$L\gamma_5$	L ₂ -N ₁		
$K\beta_4^I$	K-M ₂	$L\beta_5$	L ₃ -O _{4,5}	$L\gamma_6$	L ₂ -O ₄		
$K\beta_4^{II}$	K-N ₅	$L\beta_6$	L ₃ -N ₁	$L\gamma_8$	L ₂ -O ₁		
$K\beta_{4x}$	K-N ₄	$L\beta_7$	L ₃ -O ₁	$L\gamma_8'$	L ₂ -N ₆₍₇₎		
$K\beta_5^I$	K-M ₅	$L\beta_7'$	L ₃ -N _{6,7}	$L\eta$	L ₂ -M ₁		
$K\beta_5^{II}$	K-M ₄	$L\beta_9$	L ₁ -M ₅	$L\iota$	L ₃ -M ₁		
		$L\beta_{10}$	L ₁ -M ₄	$L\varsigma$	L ₃ -M ₃		
		$L\beta_{15}$	L ₃ -N ₄	$L\tau$	L ₃ -M ₂		
		$L\beta_{17}$	L ₂ -M ₃	$L\upsilon$	L ₃ -N _{6,7}		
				$L\nu$	L ₂ -N ₆₍₇₎		

In the case of unresolved lines, such as K-L₂ and K-L₃, the recommended IUPAC Notation is K-L_{2,3}.

The principles laid down for X-ray levels, and X-ray emission lines, should also be followed when the states involved are not X-ray diagram levels. Since the Siegbahn nomenclature applies also to lines which do not have level designations it was originally desired that the IUPAC nomenclature should contain special rules for this purpose. Such a set of rules creates several problems which are best exemplified by considering $K\alpha$ high-energy satellites for which the level assignments are known. The Siegbahn system contains satellite lines named from $K\alpha_3$ to $K\alpha_{11}$ in addition to lines named $K\alpha'$, $K\alpha''$, $K\alpha_3'$, $K\alpha_3''$ etc.

Theory predicts many more lines than are seen experimentally. Some lines are unresolved only in certain elements, and some lines are ordered differently in different elements. Although the level notation is cumbersome for satellites, particularly if it is written out in full, any simple descriptive system would soon acquire the same

deficiencies as the present Siegbahn notation. Such a system would serve a purpose only if

- (i) the information required for the level notation is not available and
- (ii) there is no previous name in the Siegbahn nomenclature.

For this limited case the following naming procedure has been proposed:

Satellites of obscure origin are labelled according to the closest structure which has already been given a level designation. In the following this structure is referred to as the *main line*. It may very well be a non-diagram line. The level designation of the main line is preceded by sat_n where n is an integer or decimal number. The number n is assigned after the following rules:

1. Integer numbers are assigned in order according to the energetic separation from the main line.
2. Positive numbers are given to high-energy structures, negative numbers to low-energy structures.
3. Previous assignments for the same type of spectra take precedence.
4. In the case where additional assignments have to be made to this system, decimal numbers may be used.

This system has disadvantages and at present, it is unlikely to be widely applied. Empirical investigations of satellite structure without simultaneous level assignments are seldom performed today. A need for this kind of system would appear, however, when structures without level assignments interfere in analytical applications of X-ray emission spectroscopy.

The ordinary *Auger electron* emission process may be viewed as a radiation-less decay of a singly ionized X-ray level into a level described by two vacancies and one electron in the continuum. Disregarding the continuum, Auger electron emission is thus a transition from a singly to a doubly ionized X-ray level. The conventional notation for Auger emission lines and bands is based upon this concept and the level notation above. In order to conform with the present IUPAC Notation of X-ray spectra the hyphen separating initial and final-state levels should be introduced also into the Auger electron notation. IUPAC thus recommends writing, e.g., $\text{K-L}_1\text{L}_{2,3}$ instead of $\text{KL}_1\text{L}_{2,3}$.

The IUPAC Notation for X-ray spectra can be extended easily to *photoelectron spectroscopy*. Since the physical process is the same, and the difference from X-ray absorption lies in the recording process, one would thus obtain the same nomenclature as for X-ray absorption with the expelled electron disregarded, e.g. X-K. The current practice is to denote photoelectron lines by either the final-state level or by the orbital

notation, i.e. K or Ls. There is no risk of confusion with this practice and there is no need for changes in this area.

10.3.4.8.4 Units and conversion factors

The SI units for X-ray wavelengths are the nanometre (nm) and the picometre (pm) with $1 \text{ nm} = 10^{-9}$ and $1 \text{ pm} = 10^{-12}$ m. However, the commonly used metric unit for X-ray wavelengths is the angstrom with $1 \text{ \AA} = 10^{-10}$ m. Siegbahn introduced the X-unit in 1919, and it soon became the practical unit for X-ray wavelengths. It was chosen as 10^{-3} \AA but was implicitly defined from the value 3029.04 Xu for the lattice constant of crystalline calcite at 18°C. This definition however turned out to be insufficient since relative measurements of X-ray wavelengths could be made with higher precision than absolute determinations and since lattice constants may differ between different samples of the same crystal. For this reason X-ray spectra were calibrated against X-ray emission lines which had been determined with high precision. Two such lines were used, Cu K-L₃ (K α_1) with the wavelength $\lambda = 1537.400$ Xu [17] and Mo, K-L₃ (K α_1) with $\lambda = 707.831$ Xu [18]. After investigating several lines as possible wavelength standards, Bearden in 1965 defined a new practical angstrom unit for X-ray wavelengths written \AA^* from $\lambda = 0.2090100 \text{ \AA}^*$ for W, K-L₃ emission [19]. Recent high-precision determinations of the X-ray wavelength scale have made both the X-unit and the \AA^* obsolete [20]. The use of \AA^* is discouraged.

Conversion factors between X-units and \AA^* on the one hand and metric units on the other have been obtained from accurate measurements of X-ray wavelengths in terms of optical standards. The most accurate results currently available are from the U.S. National Bureau of Standards [21], namely

Lines	$\lambda/\text{\AA}$	Standard deviation
Cu K-L ₃	1.5405974	0.0000015
Mo K-L ₃	0.7093184	0.0000004
W K-L ₃	0.20901349	0.00000019

The combination of these values with those used to define the Xu and \AA^* scales gives the following conversion factors.

In the X-ray scale for which $\lambda (\text{Cu K-L}_3) = 1.5374000 \text{ kXu}$
 $\text{\AA} = 1.0020797(10) \text{ \AA/kXu} = 100.20797(10) \text{ pm/kXu}$

In the X-ray scale for which $\lambda (\text{Mo K-L}_3) = 0.707831 \text{ kXu}$
 $\text{\AA} = 1.0021013(6) \text{ \AA/kXu} = 100.21013(6) \text{ pm/kXu}$

The conversion factor from the \AA^* emerges as
 $\text{\AA}^* = 1.0000167(9) \text{ \AA/\AA}^* = 100.00167(9) \text{ pm/\AA}^*$

The numbers in parenthesis are the standard deviations in the last digits of the quoted values. According to the 1973 least-squares adjustment of fundamental constants [20] the energy-wavelength conversion factor is

$$hc = 1.2398520(32) 10^{-6} \text{ eV.m} = 1.986447461 \times 10^{-25} \text{ J.m.}$$

The error given here is the standard-deviation uncertainty computed on the basis of internal consistency.