Part VIII. Nomenclature system for X-ray spectroscopy

(Recommendations 1991)

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1. INTRODUCTION

This document is the eighth in a series on the nomenclature for spectrochemical analysis issued by IUPAC. Part IV is concerned with spectroscopy in the X-ray region and deals with the nomenclature, symbols and units related to X-ray emission spectroscopy and its application to quantitative analysis. No particular attention to the nomenclature of X-ray spectra was given in that document. This is instead the topic of the present document.

The nomenclature used for X-ray emission spectra was introduced by M. Siegbahn in the 1920's and is based upon the relative intensity of lines from different series. It gives no information about the origin of these lines. Since it was introduced, a number of lines have been observed which have not been classified within the Siegbahn nomenclature, particularly for the M and N series. Another problem is that its unsystematic nature makes the nomenclature difficult to learn. Many spectroscopists agree upon the need for a new and more systematic nomenclature for X-ray emission spectra. The aim of this document is therefore to present a new notation for X-ray emission lines and absorption edges to be called the IUPAC Notation. Surveys among X-ray spectroscopists have indicated a desire to have the existing Siegbahn nomenclature replaced 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.

The present document, in addition, gives units and conversion factors for X-ray wavelengths and energies.

2. TERMS CURRENTLY USED TO DESCRIBE X-RAY SPECTRA

2.1 X-ray radiation

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 excitations 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 article-induced X-ray emission (PIXE).

Emission of photons in the X-ray wavelength region also occurs from ionized gases or plasmas at high temperatures, from nuclear processes (low-energy end of the gamma-ray spectrum), and from radiative transitions between muonic states. In the following we will be concerned primarily with characteristic X-ray emission following electron or photon excitation.

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

2.2 X-ray levels

The electronic states occurring as initial and final states of a process involving the absorption or emission of X-ray radiation are called <u>X-ray levels</u>. 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, <u>configuration,</u> <u>term</u> and <u>level</u>. 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 <u>term</u> 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.

<u>Normal X-ray levels</u> or <u>diagram levels</u> 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 <u>valence levels</u> and <u>core levels</u> according to the nature of the electron vacancy.

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

X-ray levels have various degrees of ionization – single, double or higher – and may in some cases also be electrically neutral. An <u>excitation level</u> also called <u>exciton</u> 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 <u>Rydberg series</u>.

<u>Multiply ionized and excited</u> levels may be produced by many-electron processes often called <u>electron relaxation processes</u> and which leads to <u>electron shake-off</u> or secondary ionization. <u>Electron relaxation</u> also produces <u>electron shake-up</u>, 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 <u>Fermi</u> <u>level</u>. In the latter case, level energies are often referred to as <u>electron binding energies</u>. The problem of defining the reference level in insulating solids is non-trivial.

2.3 Selection rules

X-ray emission and absorption follow the <u>selection rules</u> for emission and absorption of electromagnetic radiation. These are the electric dipole selection rules leading to most intense lines, 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 <u>multipole lines</u> or forbidden lines. The use of the latter term is discouraged.

2.4 X-ray absorption

An X-ray absorption spectrum observed at low resolution consists of one or several <u>absorption continua</u> terminated at their low energy by <u>absorption edges</u> or <u>limits</u> below which the <u>photoabsorption coefficient</u> is significantly lower. The absorption limit represents the minimum

energy required to excite an electron from a given one-electron state. The nature of the absorption limits varies with the nature of the system investigated. In some gases and in insulators it represents a transition to an excitation level, while in metals it represents the transition to the bottom of the conduction energy band.

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).

2.5 X-ray emission

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 satellites 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.

3.   PRINCIPLES OF THE IUPAC NOTATION

3.1 X-ray levels

<u>X-ray levels</u> are defined as those states which occur as initial and/or final states in X-ray transitions. <u>Diagram levels</u> are those which can be described by the removal of one electron from a closed-shell electron configuration. Table 1 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. 1a shows schematically the ordering of X-ray levels. Fig. 1b shows the ordering of one-electron levels. It is recommended that one electron levels are denoted by the orbital notation ($1s$, $2s$, $2p_{1/2}$ etc.). The importance of separating the two kinds of notation will be further exemplified in Sect. 3.2 (Compare also L. G. Parratt, Rev. Mod. Phys. <u>31</u>, 616 (1959)).

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 L_2 and L_3)

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.

States with double or multiple vacancies should be denoted by:

K_2 $1s^{-2}$

KL_1 $1s^{-1} 2s^{-1}$

$L^n_{2,3}$ $2p^{-n}$
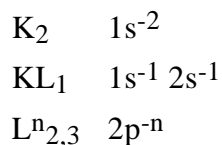
Due to electron interaction this notation does not in general give a complete description of the level structure. When desired one may therefore add the electronic term symbol of atomic or molecular spectroscopy in parenthesis after the level symbol, e.g. KL_1 (^1S) or KL_1 (^3S).

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 double ionized state KL_1.

3.2 X-ray transitions

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 in Sec. 3.1. 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.

Table VIII.1. Correspondence between X-ray diagram levels and electron configuration

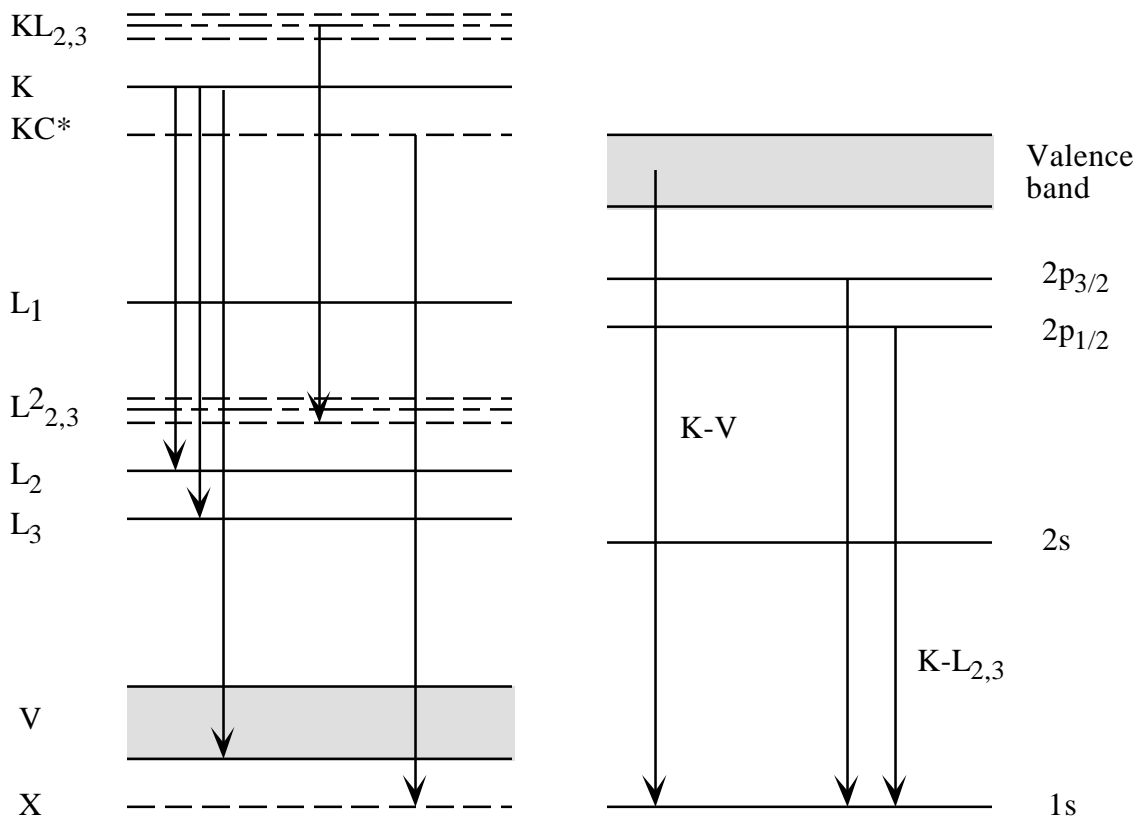| level	electron Configuration	level	electron Configuration	level	electron Configuration
K	$1s^{-1}$	N_1	$4s^{-1}$	O_1	$5s^{-1}$
L_1	$2s^{-1}$	N_2	$4p_{1/2}^{-1}$	O_2	$5p_{1/2}^{-1}$
L_2	$2p_{1/2}^{-1}$	N_3	$4p_{3/2}^{-1}$	O_3	$5p_{3/2}^{-1}$
L_3	$2p_{3/2}^{-1}$	N_4	$4d_{3/2}^{-1}$	O_4	$5d_{3/2}^{-1}$
M_1	$3s^{-1}$	N_5	$4d_{5/2}^{-1}$	O_5	$5d_{5/2}^{-1}$
M_2	$3p_{1/2}^{-1}$	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	$3d_{5/2}^{-1}$				

Figure VIII.1a. A schematic X-ray level diagram. Non-diagram levels and transitions are indicated by dashed lines. (Not drawn to scale).

Figure VIII.1b. The corresponding one-electron energy level diagram with diagram transitions indicated.

3.2.1 X-ray absorption

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 —> 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.

3.2.2 X-ray emission

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-L_3 (Ka_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 $^2P_{3/2}$ —> 1s.

K-V (for elements and compounds of Na to Cl previously denoted by Kb_1, Kb', Kb'' 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 Sect.4.

3.2.3 Special notation for X-ray emission satellites

The principles laid down for X-ray levels, Sect. 3.1 and X-ray emission lines, Sect. 3.2.2. 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~ high-energy satellites for which the level assignments are known. The Siegbahn system contains satellite lines named from Ka_3 to Ka_{11} in addition to lines named Ka', Ka'', Ka'_3, Ka''_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 labeled according to the closest structure which has already been given a level designation. In the following this structure is referred to as the <u>main line</u>. 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 spectro-scopy .

3.3 Auger electron emission

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 of Sect. 3.1. 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., $K-L_1L_{2,3}$ instead of $KL_1L_{2,3}$

3.4 Photoelectron spectroscopy

The IUPAC X-ray notation 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 1s. There is no risk of confusion with this practice and there is not need for changes in this area.

4. CORRESPONDENCE BETWEEN THE SIEGBAHN AND IUPAC NOTATIONS

The IUPAC Notation is compared with the Siegbahn notation in the following table.

Table VIII.2. Correspondence between Siegbahn and IUPAC notation diagram lines

Siegbahn	IUPAC	Siegbahn	IUPAC	Siegbahn	IUPAC	Siegbahn	IUPAC
Ka_1	K-L$_3$	La_1	L$_3$-M$_5$	Lg_1	L$_2$-N$_4$	Ma_1	M$_5$-N$_7$
Ka_2	K-L$_2$	La_2	L$_3$-M$_4$	Lg_2	L$_1$-N$_2$	Ma_2	M$_5$-N$_6$
Kb_1	K-M$_3$	Lb_1	L$_2$-M$_4$	Lg_3	L$_1$-N$_3$	Mb	M$_4$-N$_6$
K$^I b_2$	K-N$_3$	Lb_2	L$_3$-N$_5$	Lg_4	L$_1$-O$_3$	Mg	M$_3$-N$_5$
K$^{II} b_2$	K-N$_2$	Lb_3	L$_1$-M$_3$	Lg_4'	L$_1$-O$_2$	Mz	M$_{4,5}$-N$_{2,3}$
Kb_3	K-M$_2$	Lb_4	L$_1$-M$_2$	Lg_5	L$_2$-N$_1$		
K$^I b_4$	K-N$_5$	Lb_5	L$_3$-O$_{4,5}$	Lg_6	L$_2$-O$_4$		
K$^{II} b_4$	K-N$_4$	Lb_6	L$_3$-N$_1$	Lg_8	L$_2$-O$_1$		
Kb_{4x}	K-N$_4$	Lb_7	L$_3$-O$_1$	Lg_8'	L$_2$-N$_{6(7)}$		
K$^I b_5$	K-M$_5$	Lb_7'	L$_3$-N$_{6,7}$	Lh	L$_2$-M$_1$		
K$^{II} b_5$	K-M$_4$	Lb_9	L$_1$-M$_5$	Ll	L$_3$-M$_1$		
		Lb_{10}	L$_1$-M$_4$	Ls	L$_3$-M$_3$		
		Lb_{15}	L$_3$-N$_4$	Lt	L$_3$-M$_2$		
		Lb_{17}	L$_2$-M$_3$	Lu	L$_3$-N$_{6,7}$		
				Lv	L$_2$-N$_{6(7)}$		

In the case of unresolved lines, such as K-L$_2$ and K-L$_3$, the recommended IUPAC notation is K-L$_{2,3}$

5. UNITS AND CONVERSION FACTORS

5.1 Units

The SI units for X-ray wavelengths are the nanometre (nm) and the picometre (pm) with 1 nm = 10^{-9} m and 1 pm = 10^{-12} m. However, the commonly used metric unit for X-ray wavelengths is the angstrom with 1 Å $=10^{-10}$ m. Siegbahn introduced the X-unit in 1919, and it soon became the practical unit for X-ray wavelengths. It was chosen as 10 Å 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-L$_3$ (Ka_1) with the wavelength l = 1537.400 Xu (Ref. 1) and Mo K-L$_3$ (Ka_1) with l = 707.831 Xu (Ref. 2). After investigating several lines as possible wavelength standards, Bearden in 1965 defined a new practical angstrom unit for X-ray wavelengths written Å* from A = 0.2090100 Å* for W K-L$_3$ emission (Ref.3). Recent high-precision determinations of the X-ray wavelength scale have made both the X-unit and the Å* obsolete (Ref. 4). The use of Å* is discouraged.

5.2 Conversion factors

Conversion factors between X-units and Å* 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 (Ref. 4), namely

Lines	l/Å	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 Å* scales gives the following conversion factors:

In the X-ray scale for which l (Cu K-L$_3$) = 1.5374000 kXu

$$L = 1.0020797(10) \text{ Å/kXu} = 100.20797(10) \text{ pm/kXu}$$

In the X-ray scale for which l (Mo K-L$_3$) = 0.707831 kXu

$$L = 1.0021013(6) \text{ Å/kXu} = 100.21013(6) \text{ pm/kXu}$$

The conversion factor from the Å* emerges as

$$L^* = 1.0000167(9) \text{ Å/Å}^* = 100.00167(9) \text{ pm/Å}^*$$

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 (Ref. 5) the energy wavelength conversion factor is

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

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

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