

X-Ray Emission Spectroscopy, Methods

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Symbols

d grating constant
 I_A fluorescence line intensity of an investigated element A
 I_{st} fluorescence intensity of a standard
 n order of spectrum
 p_A probability of a vacancy being filled without emission
 p_r probability of photon emission when vacancy is filled

U X-ray tube voltage
 V_i ionization potential of the i th level
 Z atomic number
 ϵ electron kinetic energy
 λ wavelength
 δ shielding constant
 φ angle of incidence

General Characteristics

Development of the theory of the electronic structure of chemical compounds has revealed a great need for physical experimental methods to which modern methods of quantum chemistry can be applied. Primary information provided by quantum chemical methods of electronic structure studies concerns the energy spectrum of molecules as well as the structures of wavefunctions of molecular orbitals (MOs). There is a need for physical methods which would allow direct measurement of MO energies as well as the determination of the degree of participation of different atomic electrons in chemical bonding. X-ray emission spectroscopy (XES), which provides both integral information about electronic structure (effective charges on atoms, atomic orbital populations) and differential information (relative energies of occupied MOs and characteristics of their AO components), can be seen as an important approach.

X-rays, discovered by Röntgen in 1895, are a form of electromagnetic radiation that occupies the spectral area between UV and γ radiation in the range of wavelength $\lambda=10^{-3}-10^2$ nm, corresponding to energies $h\nu=10-10^6$ eV ($v=c/\lambda$). X-ray spectroscopy is divided into X-ray emission and X-ray absorption spectroscopy and is subclassified into short wavelength ($\lambda\leq 0.2$ nm), long wavelength ($0.2\leq\lambda\leq 2$ nm) and ultralong wavelength ($\lambda>2$ nm) regions.

X-ray emission spectroscopy is used for the study of electronic structure and for the qualitative and quantitative analysis of substances. With the help of X-ray emission spectroscopy one may investigate all elements of the periodic table (with $Z>2$) in compounds and in any phase.

X-rays are divided into continuous and characteristic. Continuous X-rays occur as a result of the stopping of very fast charged particles (e.g. electrons) in the target substance and have a 'white' spectrum. Characteristic X-ray emission radiation is emitted by target atoms after their collisions with hot electrons (primary excitation) or with X-ray photons (secondary excitation, fluorescence radiation) and produces a

line spectrum. These collisions may also remove an electron of any inner shell of a target atom. The resulting vacancy is filled by an electron transition from another inner or outer electron shell. As a consequence of this electron transition, energy is released which may be in the form of an X-ray quantum (Figure 1).

Characteristic X-Ray Emission Spectra

Characteristic X-ray emission spectra consist of spectral series (K, L, M, N...), whose lines have a common initial state with the vacancy in the inner level. Labels of basic X-ray transitions are shown in Figure 2. All electron levels with the principal quantum number n equal to 1, 2, 3, 4, etc. are named as K, L, M, N etc. levels and denoted with corresponding Greek letters and digit indexes. The electron transitions which satisfy the dipole selection rules

$$\Delta l = 1; \Delta j = 0, 1 \left(j = \pm \frac{1}{2} \right); \Delta n \neq 0 \quad [1]$$

are most intense. The dependence of X-ray emission line energy on atomic number Z is defined by Moseley's law:

$$h\nu \sim (Z - \sigma)^2 \quad [2]$$

where Z is the atomic number and σ is the shielding constant, which varies from series to series. Therefore, any X-ray emission spectral line is the finger-print of an element.

With X-ray emission excitation by electron bombardment (primary emission) all emission lines of the i th series appear when the X-ray tube voltage U exceeds the ionization potential

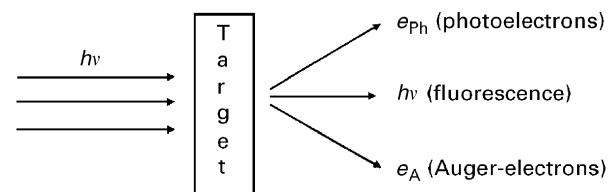


Figure 1 Scheme of radiation interaction with a substance.

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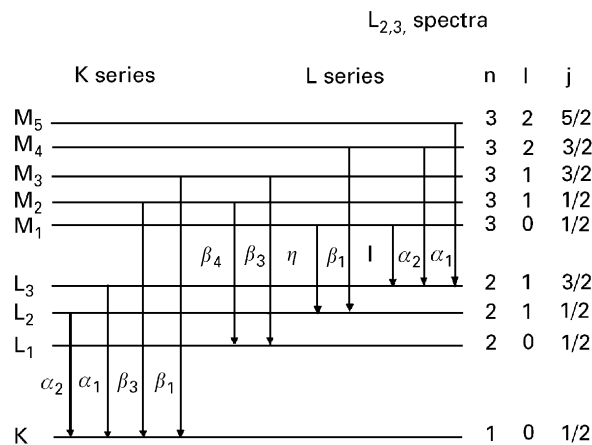


Figure 2 Scheme of the most important X-ray emission transitions; n , l and j are correspondingly the principal, orbital and total quantum numbers of K, L₁, L₂, L₃ levels, etc.

of the i th level (V_i). At higher U the intensity of all lines of the i th series, I_i , increases because the electrons penetrate deeper into the target substance and, therefore, the number of excited atoms in the target increases. In the $V_i < U < 3V_i$ region, the intensity obeys the rule $I_i \sim (U - V_i)^{-2}$. With a further increase in U X-ray emission begins to be absorbed by the target atoms; therefore the increase in I_i is reduced. At $U \geq 11 V_i$, I_i decreases because now most of the excited atoms are so deep in the target that their emitted radiation is absorbed by the target substance.

X-ray emission spectra are usually excited by X-ray photons because most chemical compounds are decomposed by electron bombardment. With X-ray emission spectra excitation by photons [secondary emission or fluorescence (XFS)] the fluorescent line intensity depends on the exciting photon energy $h\nu$ and $I_i = 0$ if $h\nu < V_i$. All lines of the i th series appear if $h\nu = V_i$; however, I_i decreases little with further increase in $h\nu$. Therefore, to excite X-ray fluorescence one must use a target that contains a substance with intense characteristic X-ray lines whose energy just exceeds eV_i . Using the continuous radiation of an X-ray tube with a target consisting mostly of heavy elements it is possible to excite X-ray fluorescence.

The intensity of a characteristic X-ray spectrum (both primary and fluorescent) depends on the probability p_i of a radiation transition in the atom having the vacancy in the i th level. The value of p_i is determined by the total probability of photon emission when this vacancy is filled by outer electrons. However, with a probability p_A the vacancy may be filled by outer electrons without radiation as the result of the Auger-effect (see Figure 1). For the K series of medium and heavy elements $p_i > p_A$, for the light elements $p_i < p_A$. For all other series of any elements $p_i \ll p_A$. The ratio $f = p_i / (p_i + p_A)$ is called the yield of characteristic radiation.

However, X-ray characteristic lines appear because of single atom ionization; in X-ray emission spectra weaker lines are found to occur as a result of binary (or multiple) atom ionization when two (or more) vacancies are formed simultaneously in different electron shells. If, for example, one vacancy is formed in the K shell of atoms and filled by electrons belonging to the L_{2,3} shell, atoms emit an $\tilde{E}\alpha_{1,2}$ doublet. If another vacancy is formed simultaneously which too is filled by

electrons from the L_{2,3} shell, then the final state will have a binary ionization L_{2,3}L_{2,3}, and would correspond to the emission of radiation with energy exceeding that of the $\tilde{E}\alpha_{1,2}$ doublet. As a result, in an X-ray emission, spectrum a short wavelength $\tilde{E}\alpha_{3,4}$ doublet, called a satellite of the main $\tilde{E}\alpha_{1,2}$ doublet, would appear. Because of such processes of multiple ionization X-ray emission, spectra may have a large number of satellites of the main lines. Usually, the satellite intensity is some orders of magnitude less than that of the main lines. However, if target atoms are bombarded by heavy ions with great energy, the probability of multiple atom ionization becomes higher than that of single ionization. Therefore, in this case the intensity of the main emission lines is essentially less than that of the satellites.

The Continuous X-Ray Spectrum

The continuous X-ray radiation occurs because of electron deceleration in the target substance. Electron energy losses by radiation have quantum character, the emitted photon having an energy $h\nu$, which cannot exceed the electron kinetic energy ε , i.e. $h\nu \leq \varepsilon$. The energy $h\nu_i = \varepsilon$ is called the quantum boundary of a continuous spectrum. The corresponding wavelength λ_i depends on the X-ray tube voltage charge U as follows:

$$\lambda_i(\text{nm}) = hc/(eU) = 1239.8/U(V) \quad [3]$$

At $\lambda < \lambda_i$ the intensity of continuous radiation is absent. With an increase in λ from λ_i to $3\lambda_i/2$ the continuous radiation intensity increases and with further increases in λ it decreases.

X-Ray Sources

The most widespread source of X-rays is the X-ray tube. In an X-ray tube, electrons emitted from the cathode are accelerated by an electrical field and bombard the metal target (anode). Target atoms, excited by electron impact, and electrons losing their kinetic energy when decelerating in the anode substance, emit X-rays. The primary radiation of the X-ray tube consists of two parts – characteristic (line) and continuous radiation. As a result of the primary radiation impinging on a substance its atoms emit characteristic fluorescence (secondary) radiation.

Other sources of X-rays are radioactive isotopes which can directly emit X-rays or electrons or particles. In the last two cases charged particles can bombard the target substance which then emits X-rays. The intensity of X-ray isotope sources is some orders of magnitude less than that of X-ray tubes; however the dimensions, weight and cost of X-ray isotope sources are less than that of X-ray tubes.

X-rays are also generated as synchrotron radiation. It can be selected by a crystal analyser and may be used as an X-ray source. The intensity of X-rays selected from synchrotron radiation is some orders higher than that from an X-ray tube.

The characteristic radiation of the X-ray tube is spread in space isotropically, whereas its continuous radiation has maximal intensity in directions in a plane perpendicular to the trajectory of electrons bombarding the target. The X-ray

component of synchrotron radiation is polarized and spread only in the plane of the synchrotron ring.

Obtaining X-Ray Emission Spectra

A schematic of an X-ray fluorescence instrument is presented in Figure 3. The X-ray tube is used as the source of primary radiation $h\nu_1$. The vacancies in inner shells of atoms of the substance investigated are formed as a result of primary radiation action. These vacancies are filled by other inner or outer electrons. This is accompanied by X-ray fluorescent photons $h\nu_2$ being emitted. This fluorescence radiation is spread out into the spectrum by means of a crystal analyser (or, for the ultrasoft X-ray region, by means of diffraction gratings) in accordance with Bragg's law

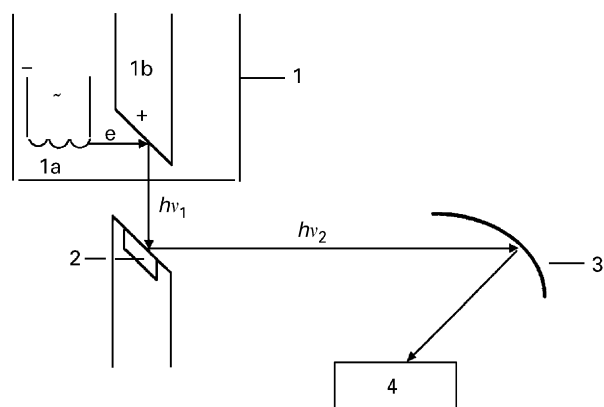


Figure 3 An X-ray fluorescence spectrometer. 1, X-ray tube; 1a, electron source; 1b, target; 2, substance investigated (secondary anode); 3, crystal analyser; 4, registration device; $h\nu_1$, primary radiation; $h\nu_2$, secondary radiation; and $h\nu_3$, registered radiation.

$$2d \sin \varphi = n\lambda \quad [4]$$

where n is the order of the spectrum, λ is the wavelength, d is the grating constant of the crystal analyser and φ is the angle of incidence of the collimated X-ray fluorescent beam on the specific set of parallel planes in the crystal from which the beam is diffracted (see Table 1).

The X-ray fluorescence spectrum is then registered on a photographic film or by Geiger, proportional or scintillation counters, semiconductor detectors, etc. The wavelengths and energies of the characteristic emission lines have been accurately measured and tabulated in handbooks, monographs and reference works for all chemical elements with $Z > 2$.

X-Ray Fluorescence Analysis

X-ray fluorescence analysis (XFA) is based on the X-ray emission line's intensity dependence on the concentration of the appropriate element. XFA is widely used for the quantitative analysis of various materials, especially in black and colour metallurgy and geology. XFA is distinguished by rapidity and

a high degree of automation. The detection limits depend on the element, matrix composition and spectrometer used and lie in the region 10^{-3} – $10^{-10}\%$. Defining any element (with $Z > 4$) is possible by means of XFA in both a solid and a liquid phase.

However, the fluorescence line intensity I_A of an investigated element A depends not only on its concentration C_A in the sample, but also on the concentration of other elements, C_i , because other elements promote both absorption and excitation of fluorescence of the element A (matrix effect). Moreover, the measured value I_A essentially depends on the sample surface, phase distribution, grain sizes, etc. Numerous methods have been developed to account for such effects. Most notable are the empirical methods of external and internal standards, using the background of scattered primary radiation and the method of dilution.

In the external standard method the unknown concentration C_A of the element A is determined by comparing the intensity I_A in the sample investigated with analogous I_{st} values of standards for which defined element concentrations C_{st} are known:

$$C_A = C_{st} I_A / I_{st} \quad [5]$$

This method allows one to take into account corrections connected with the equipment used; however, the composition of the standard should be close to that of the investigated sample to precisely match the matrix effect.

In the internal standard method some amount $\Delta N_{\sim A}$ of a defined element A is added to the sample investigated. This leads to an increase in the fluorescence intensity of ΔI_A . In this case:

$$C_A = I_A \Delta C_A / \Delta I_A \quad [6]$$

Table 1 Parameters of typical crystal analysers

| Crystal | Reflecting plane | 2d (nm) | Maximal resolving ability ($\lambda/\Delta\lambda$) | Relative coefficient |
|----------|------------------|----------|---|----------------------|
| KAP | 001 | 2.7714 | 1400 | 8–18 |
| Mica | 002 | 1.9884 | 2000 | 2–3 |
| ADP | 101 | 1.0659 | 10 000 | 1–10 |
| EDDT | 020 | 0.8808 | – | – |
| PET | 002 | 0.8726 | 8000 | 10–20 |
| Quartz | 1010 | 0.8512 | 20000 | 1–10 |
| Quartz | 101 1 | 0.671 53 | 10 000 | 2–14 |
| Plumbago | 002 | 0.6696 | 100 | 50–200 |
| Ge | 111 | 0.653 27 | 6000 | – |
| Si | 111 | 0.6271 | 10 000 | 2–10 |
| Calcite | 211 | 0.6069 | 15 000 | 2–30 |
| Quartz | 1020 | 0.4912 | 30 000 | 0.4–3.3 |
| LiF | 200 | 0.4028 | 2000 | 10 |
| Ge | 220 | 0.400 | 13 000 | 17–23 |
| Si | 220 | 0.383 99 | 29 000 | 1–6 |
| Calcite | 422 | 0.3034 | 64 000 | 0.4–0.9 |
| LiF | 220 | 0.2848 | 1300 | 10–20 |
| Quartz | 202 3 | 0.2806 | 90 000 | 0.3–0.9 |
| Quartz | 224 3 | 0.2024 | 144 000 | 0.2–0.45 |
| Calcite | 633 | 0.202 | 122 000 | 0.3–0.6 |

This method is especially effective for the analysis of complex samples but needs the special requirements of sample preparation.

The use of the background of scattered primary radiation is based on the fact that the ratio $I_A:I_b$ (I_b is the background intensity) mainly depends on C_A and only weakly depends on the concentration of other elements, C_i .

In the method of dilution a great amount of a weak absorber or a small amount of strong absorber is added to the sample investigated. These additions should reduce the matrix effect. This method is effective for water solution analysis and for the analysis of complex samples when the internal standard method is inapplicable.

There are also models in which the measured intensity I_A is corrected on the basis of the intensities I_i and concentrations C_i of other elements. For example, C_A may be represented as:

$$C_A = a_{A0} + a_{A1}I_A + a_{A2}I_A^2 + I_A \sum_{m,i} m_{Ai}I_i + \sum_{m,i} b_{Ai}I_i + \sum_{m,i} d_{Ai}I_i^2 (i \neq A) \quad [7]$$

where a and b are values determined by the least-squares method with the help of I_A and I_i values measured in several standards with known concentrations C_A of element A. Such models are widely used for the computerized serial analysis of many samples.

X-Ray Microanalysis

X-ray microanalysis is a local analysis, fulfilled by means of a microanalyzer electron probe, for sample sites of $\sim 1\text{--}3\text{ }\mu\text{m}^2$.

The electron probe is formed by electrostatic and magnetic fields to obtain a parallel electron beam with a diameter of $\sim 1\text{ }\mu\text{m}$. The analysis is via primary X-ray sample emission which is spread out into a spectrum by means of the X-ray spectrometer. In this method corrections for the atomic number of the element, the absorption of its radiation in the sample, its fluorescence, and the characteristic spectra of other elements contained in the sample must be accounted for. Microanalysis is used for the investigation of two- and three-component systems such as mutual diffusion, crystallization processes, local variations of alloy structure, etc.

See also: X-Ray Emission Spectroscopy, Applications; X-Ray Fluorescence Spectrometers; X-Ray Fluorescence Spectroscopy, Applications; X-Ray Spectroscopy, Theory.

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