

Review Paper on High Energy K X-RAY Satellites

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Abstract

This study focus on High Energy K X-ray satellites which are a particular category of characteristic X-ray. They are emitted when an atom that has undergone multiple ionization de excites. Simultaneous single ionization in the K-shell and multiple ionization in the L-shell gives rise to K_{α} X-ray satellites. These can be studied only by high energy resolution instruments like crystal spectrometry. Experimental investigations were carried out in this field by several workers using photon, electron, and ion excitation modes. The theoretical models to predict their energies and intensities were developed. And also this work can show a clear discrepancy between theoretical and experimental results in the case of satellites formation from different shells. In case of experimental instrumentation, WDXRF is the most accurate for determining the energy and intensity of X-ray satellites. The basic source of data was literature done by different scholars.

Keywords: X-ray satellites; spectrometers; energy ratio; intensity ratio

1. INTRODUCTION

X-ray spectroscopy has developed over the years in to a powerful analytical tool with applications in a wide range of fields like elemental analysis, study of chemical structure, X-ray astronomy, plasma physics etc. All aspects of X-ray spectra should be understood in the finest detail possible to achieve maximum accuracy in such analytical studies. Investigation of X-ray satellites helps to further our understanding of inner shell ionization. Basically this is happen when an atom ionized simultaneously in different shells de-excites, X-ray satellites are produced. The K_{α} X-ray satellites or non-diagram lines were first observed by electron bombardment by Siegbahn and Stenstrom¹. Wentzel² was the first to interpret these lines as arising from multi-ionized atoms having one or more L-shell vacancies in addition to one K-shell vacancy. The absence of L-shell electrons reduces the screening of the nuclear potential felt by the remaining electrons and increases their binding energies. K X-rays emitted due to transitions of electrons from such states will be at higher energies than the normal diagram line KL^0 and such lines are called $K\alpha$ satellite lines. Depending on the number of L-shell vacancies in addition to a single K-shell vacancy, these satellites are designated as $K_{\alpha}L^1(K_{\alpha}L)$, $K_{\alpha}L^2(K_{\alpha}LL)$, $K_{\alpha}L^3(K_{\alpha}LLL)$, ..., $K_{\alpha}L^n(K_{\alpha}LLL \dots nL)$ (where n is the number of L vacancies). When $n = 0$, it represents the normal diagram line $K\alpha L^0$ (i.e. $K_{\alpha 1\alpha 2}$). Similarly K_{β} satellites can be designated as $K_{\beta}L^1$, $K_{\beta}L^2$, ..., $K_{\beta}L^n$.

It was widely believed that K_{α} X-ray satellites or non-diagram lines found in electron excitation do not appear in fluorescent excitation³. However, later experimental work showed that this was not true^{4,5}. Further it was also concluded from measurements of charge states of ions formed following photo-ionization, that two or more electrons could be ejected with considerable probability, when one photon is absorbed⁶. In the early days for the measurement of the K_{α} X-ray satellites, photographic technique was used but subsequently crystal spectrometers in combination with continuous flow proportional counters were being used.

Several theoretical formalisms⁷ are available for computing the energy shift of $K\alpha L^1$ from the diagram line $K\alpha L^0$: (a) Non-relativistic Hartee-Fock calculations, (b) simple analytical model of Burch *et al*⁸ (c) modified version of Burch, including relativistic effects, (d) self-consistent field calculations of Bhattacharya *et al*⁹. In addition to these there is a semi-empirical formula proposed by Torok¹⁰ for the prediction of these energy shifts, later discussed under theoretical models in detail.

Generally, these paper states the production of K X-ray satellites, the correlation between experimental and theoretical results of energy shifts for different Z-values, and the dependence on mode of excitation, chemical effects and Z-systematics of relative intensity and energy shifts where the experimental results from different literature have been considered.

2. EXPERIMENTAL DETAILS

Based on the fact that, when a beam of X-rays is directed on to a sample, secondary fluorescent X-rays are emitted at a series of wavelengths characteristic of the element under investigation. The individual components of the fluorescent X-radiation are separated by means of an analyzing crystal, which diffracts them at different angles according to their wavelengths. Each wavelength refers to a different X-ray, the energy and intensity of which can be measured by means of a suitable detector placed in the appropriate position. The basic facilities needed for such investigation are, X-ray wavelength dispersive crystal spectrometer. The crystal is so oriented as to reflect only one wavelength at a given angle. By slowly rotating the crystal at one half the angular speed of

the detector, the various wavelengths from the parallel beam of target X-rays are reflected, one by one, as the crystal makes the appropriate angle for each wavelength. The intensity at each wavelength can then be measured with a suitable detector.

Description of Crystal Spectrometer: This system consists of a plane crystal, a continuous flow type proportional counter with a thin (1 micron) polypropylene window and an X-ray generator with a suitable X-ray tube (Rh X-ray tube in the present case). The system has a built-in provision to change the crystal by operating an external switch without disturbing the optimum conditions. Basically X-rays from the tube, incident on the target, produce characteristic X-rays of the target, which are made to fall on the plane crystal. The diffracted rays from the crystal are detected by the continuous flow type proportional counter maintained at a constant pressure (1atmos)¹¹.

The radiation detector and the analyzing crystal are mounted on a high precision goniometer which is an instrument used to rotate both X-ray tube and the detector from 0° to 148° (2θ) under a microprocessor control. The goniometer is driven by a stepping motor and it is possible to scan its full angular range, in either direction. The goniometer is normally made to scan from a lower angle to a higher angle. The fast bi-directional facility available enables the goniometer to be used for specific measurement at predetermined angles. In the present experiment, in order to have correct peak identification by way of angular accuracy, the goniometer is set to proceed always in the same direction to approach the selected angle. The goniometer has the facility of scanning the spectrum in 2θ steps of 0.01° to 1° with a required predetermined time setting at each position¹².

The crystal attenuator unit carries nine such terminals each related to an attenuator for a particular type of analyzing crystal, a mains connector and an earth connection. X-rays are attenuated by air, and for this reason, spectrometry is normally performed in a low vacuum. The vacuum system is designed to maintain a vacuum in the sample and crystal chambers while measurements are being made. The system consists of a vacuum pump, the air lock, the sample chamber, the crystal chamber, the air filter and three valves. The air-lock provides the means of transferring the sample to be analyzed from the loading position in the air lock to the sample turret without disturbing the vacuum. It is also provided with several interlocking and safety features to prevent faulty operation. The sample turret switch is a four position rotary with one position corresponding to each of the four samples. When the switch is set to a selected position, the sample turret will be rotated by its motor until the sample of interest is in the analyzing position.

During experimental investigations the following should be considered: Self-Absorption in the Sample:
 - To correct for such an absorption¹³, the following expression is used:

$$I = I_0(\mu_\rho t)^{-1}(1 - e^{-\mu_\rho t})$$

Where I_0 = corrected intensity, I = observed intensity, μ_ρ = Mass Absorption Coefficient of the target materials for the X-rays under study and t = thickness of the sample (gm/cm²)

$$(\mu_\rho)_{\text{compound}} = \sum_i W_i(\mu_\rho)_i$$

where, W_i is the fractional weight age and $(\mu_\rho)_i$ is the Mass Absorption Coefficient of the constituent elements; Crystal Reflectivity: - The reflectivity of the crystal depends upon the wavelength of the X-rays under analysis. This correction is carried out assuming that the reflectivity is proportional to the cube of the wavelength¹⁴. The correction for reflection is small, so the net correction is still smaller; Window Absorption: - This correction is carried out employing the basic relation for absorption

$$I_0 = Ie^{-\mu_\rho t}$$

I is the observed intensity, μ_ρ is the Mass Absorption Coefficient of the window material, t is the thickness of the window (gm/cm²); Efficiency of the Detector:- Because of the differences in the energies of X-ray lines there may be differences in the quantum counting efficiency of the counter for these energies. This efficiency is usually determined by estimating the absorption in the gas of the counter.

3. DISCUSSION: THEORETICAL COMPUTATIONS BASED ON SOME MODELS

Satellite Energies: Deutsch¹⁴ has computed the energy shift of $K_\alpha L^1$ satellite relative to $K_\alpha L^0$ diagram line using four theoretical models for the elements in the Z range 10-32. The salient features of these four models and Semi-empirical Formula of Torok *et al*¹⁵ are presented briefly as; HF- the Non-Relativistic Hartee-Fock Calculations:- In this model intermediate coupling scheme is adopted and only single configurations are employed. As the contribution of 2S spectator hole to the satellite spectrum was experimentally determined^{8, 16} to be negligible for the z range under consideration only 2p spectator hole configurations were considered. The energies for initial and final configurations were computed using MCHF₇₈ programme developed by Froese¹⁷. The satellite energy shift was calculated from the following equation:

$$\Delta E_1 = [E(1S^{-1}2P^{-1}) - E(2P^{-1})] - [E(1S^{-1}) - E(2P^{-1})],$$

where $E(nl)$ and $E(nl n'l')$ were taken as the total energy of the nl and $nl n'l'$ Configurations respectively as obtained from the programmed; B-S – the Simple Analytical Model of Burch:- In this model the

effective charge of the long lived 2p spectator vacancy is uniformly smeared over the 2p shell. This charged shell is the source of a perturbing electrostatic potential which shifts the inner levels of the atom none uniformly causing the energy shifts of the satellite line relative to the spectator less case of the diagram line. According to Burch *et al*⁸ a vacancy the 2p shell produces a perturbing potential,

$$V_{2p}(r) = r^{-1} - 4\pi r^{-1} \int \rho_{2p}(r')(R'^2 - rr')dr',$$

(where an integral tends from $r \rightarrow \infty$) where using hydrogen like wave functions,

$$\rho_{2p}(r) = \psi_{2p}^2(r) \propto r^2 \exp(-Zer)$$

After integration and normalization (by checking using $\frac{\partial^2 V}{\partial r^2} = -4\pi\rho$ above $V_{2p}(r)$ equation will have)

$$V_{2p}(x) = \left(\frac{Ze}{x}\right) \left[1 - \frac{1}{24}e^{-x}(x^3 + 6x^2 + 18x + 24)\right],$$

Where $x = Zer/\alpha_0$. The binding energy shifts are given by

$$\Delta K = \langle 1s|V_{2p}|1s\rangle$$

$$\Delta L = \langle 2p|V_{2p}|2p\rangle$$

$$\Delta M = \langle 3p|V_{2p}|3p\rangle$$

The removal of the 2p electron increases the binding energy of each of the levels. The un shifted and shifted K X-ray energies are indicated, making no distinction between $K_{\alpha 1}$ and $K_{\alpha 2}$. We use the sudden approximation in which the transition energies are defined as difference in binding energies. From these the $K_{\alpha}L^1$ energy shift can be calculated as follows:

$$\Delta K_{\alpha}L^1 = \Delta K - \Delta L, \text{ so this model yields for the shift,}$$

$$\Delta K_{\alpha}L^1 = 1.66Ze$$

Where Z_e is the effective charge¹⁷ given by $Z_e = Z - \sigma$, where σ is the Slater¹⁸ screening constant which is taken as 4.15 for all Z; B-HF- Model:- This is a modified version of the previous model of Burch, developed by Deustch¹⁴ where relativistic effects were included and Z dependent screening constant obtained from HF calculations was used in place of the constant value of 4.15; SCF- Self Consistent Field model:- This model developed by Bhattacharya *et al*⁹ further improved version of Burch's model where analytic self-consistent field wave functions were employed in place of the screened hydrogenic functions used in all the previous models. Relativistic effects were included in this model; S-E- Semi – Empirical Formula of Torok *et al*:- This semi-empirical formula based on graphical systematic developed with an experimental data base obtained by different authors by different modes of excitation. It gives the shift as

$$\Delta E(K_{\alpha}L^1) = 1.530(Z - 6.828),$$

Where 6.828 is the screening constant taken in place of 4.15, which Torok *et al*¹⁵ claim resulted in better agreement with experimental values.

Experimental energy shifts of KL satellites and the calculated values after $\Delta(K_{\alpha}L) = 1.66Z_L = 1.66(Z - 4.15)$ ¹⁵ have a significant difference. Here $Z_L = (Z - 4.15)$ is the effective charge at the L shell determined from the Slater screening rules with i spectator holes one has to multiply this Δ value by i, shows the equation superimposed on the experimental values. At seven vacancies the agreement with the experiments is quite good. For better agreement other Z dependent effective charges were used by several authors obtaining much better agreement for single vacancy shift. These investigators did not report the application of their results for more vacancies.

From a systematic of the $K_{\alpha}L^1$ satellites and from a single spectator hole, we obtained another similar equation, again for equally spaced satellites,

$$\Delta(K_{\alpha}L) = 1.530(Z - 6.828)$$

The following simple empirical calculation (with an imposed effective Z) of the energy shift for the case of i spectator L vacancies was obtained:-

$$\Delta E(K_{\alpha}L^i) = i \times 1.530[Z + 0.5(i - 1) - 6.828]$$

$$\text{Where, } i = 1, 2, 3, \dots 7$$

In the other cases, employing the simple analytical model of Burch *et al*⁹ described above, $K_{\beta}L^1$ satellite energy shifts can be computed from,

$$\Delta K_{\beta}L^1 = \Delta K - \Delta M.$$

From that model, for hydrogen like wave functions, this turns out to be

$$\Delta K_{\beta}L^1 = 4.38Ze, \text{ (}\Delta \text{ Shifts in the binding energies)}$$

Using this relation these satellite energy shifts are computed for Z range 19-25 taking the Slater's screening constant $\sigma = 4.15$ in the relation $Ze = Z - \sigma$ and also taking $\sigma = 6.828$ as suggested by Torok *et al*¹⁵.

Table 1. Theoretical $K_{\alpha}L^1$ energy shifts^{19, 20}

Z	H.F.	B.HF.	B-S	Bh	S.E.
10	5.2	8.6	9.7	5.6	4.8
11	6.7	10.4	11.4	7.3	6.4
12	8.2	12.1	13.0	9.0	7.9
13	9.5	13.8	14.7	10.7	9.4
14	10.8	15.5	16.4	12.5	11.0
15	12.1	17.2	18.0	14.2	12.5
16	13.4	18.8	19.7	15.9	14.0
17	14.6	20.5	21.3	17.6	15.6
18	15.8	22.1	23.0	19.4	17.1
19	17.3	23.8	24.7	21.1	18.6
20	18.3	25.4	26.3	22.8	20.2
21	20.4	27.0	28.0	24.5	21.7
22	22.0	28.7	29.8	26.3	23.2
23	23.5	30.3	31.3	28.0	24.7
24	25.1	31.9	33.0	29.7	26.3
25	26.4	33.5	34.6	31.4	27.8

Table 2. Theoretical $K_{\beta}L^1$ energy shifts^{9, 19}

Atomic number	Z_e $= Z - 4.15$	$\Delta K_{\beta}L^1$	Z_e $= Z - 6.828$	$\Delta K_{\beta}L^1$
19	14.85	65.0	12.172	53.3
20	15.85	69.4	13.172	57.7
21	16.85	73.8	14.172	62.1
22	17.85	78.2	15.172	66.4
23	18.85	82.6	16.172	70.8
24	19.85	86.9	17.172	75.2
25	20.85	91.3	18.172	79.6

Satellite Relative Intensities: According to the Wentzel-Druyvesteyn theory²¹, there exists a possibility for not only one, but two or more photoelectrons being emitted from the atom in X-ray excitation. The resulting anomalous multi-hole states produce satellites while the normal single inner-hole states produce the diagram line. The Richtmeyer²² theory suggests that in the anomalous states, which produce satellites, the outer electrons of the atom are excited but are still bound to the atom. No explanation is provided in these theories as to how the anomalous states arise. Nevertheless, it is common to both the theories that some sort of an anomalous state, which corresponds to an anomalous configuration of mainly the outer electrons, is responsible for a satellite line. These anomalous states can be termed as “Valence-Electron-Configuration” (VEC) states⁵. The assumption is that the formation of an inner hole occurs so quickly that the rapid change in the Coulomb field experienced by electrons, other than the photoelectron, gives rise to the anomalous configuration. The change in the Hamiltonian, attributable to the production of an inner vacancy or hole, is regarded as a Sudden approximation. In the Sudden approximation, $W(nl)$, the relative probability for anomalous or VEC states, which are the initial states of the satellites, corresponding to an anomalous configuration of electrons originally in the nl shell, is given by

$$W(nl) = \frac{[1 - P(nl)]}{P(nl)}$$

$P(nl)$ is the probability that the electrons in shell nl stay in their orbits (keep their quantum numbers n, l, m_l, m_s) during the excitation:

$$P(nl) = \left[\int_0^{\infty} R_{nl}(r)R_{nl}^1(r)r^2 dr \right]^{2p}$$

Where, P is the number of electrons in the shell. $R_{nl}(r)$ and $R_{nl}^1(r)$ are the radial functions of the ground and the excitation state spin orbitals, respectively. The intensity ratio of the $K_{\alpha}L^n$ satellite group and the $K_{\alpha 1,2}$ line is given by

$$\frac{IK_{\alpha}L^n}{IK_{\alpha 1,2}} = \frac{f_s}{f_0} [W(2s) + W(2s)W(2p)] + \frac{5f_p}{6f_0} W(2p)$$

in which f_0 is the oscillator strength of transitions between the normal states and f_s is the mean oscillator strength of transition between anomalous states which correspond to excitation or ionization of L_I -shell electrons and L_I , L_{II} and L_{III} - shell electrons, simultaneously. The oscillator strength f_0 is assumed to change slightly when the outer electrons become excited or ionized. In the case of excited states the excitation probability can be calculated in accordance with the Sudden approximation, if

$$2\pi[W_{nl n'l'} - W_{nl}] \frac{\tau_{n'l'}}{h} \ll 1$$

Where W_{nl} is the energy of the normal single hole state, $W_{nl n'l'}$ is the energy of the anomalous state with an extra $n'l'$ and $\tau_{n'l'}$ is the time of transit of the ejected photoelectron past the $n'l'$ shell.

According to Carlson and Krause²³, the probability of the simultaneous ionization of L and K shells should be constant in photo ionization process and comparable with sudden approximation probability, if

$$(E_{KL} - E_K)t < 0.4h/2\pi$$

Here t is the time of transit of the K photoelectron past L-shell. E_{KL} and E_K are the excitation energies of the KL and K X-ray states, respectively. It can be shown that the time t in the validity criterion corresponds to an excitation energy of the incoming X-rays which is more than two times the threshold energy E_K . Based on the sudden approximation principle and assuming the Neon core and neglecting exchange effects Aberg²⁰ has calculated $\frac{K_{\alpha L^1}}{K_{\alpha L^0}}$ intensity ratio for low Z elements up to $Z = 20$.

Dependence on Mode of Excitation: No appreciable changes were observed in the energy shifts of the satellites with variation in the mode of excitation. But it was shown that relative intensity of the x-ray satellites does depend on the mode of excitation. Compared to photon excitation slightly higher relative intensity was reported by electron excitation in the elements Ti, V, Cr, and Mn (Table 3). Even in the ion mode of excitations a dependence on charge state and modes of the projectile was observed by Watson *et al*²⁴.

Projectile Dependence of Energy Shifts: The satellite energy shifts of Ti, V, Cr, and Mn between the projectiles photon and electron excitation related with other five theoretical models are listed in Table 3.

Table 3. The property of energy shift for two modes of excitation^{4, 25}

Elements	Z	Energy shift by photon excitation	Energy shift by electron excitation	HF	BS	B-HF	SCF	SE
Ti	22	25.3±1.0	28.7±0.2	22.0	29.6	28.7	26.3	23.2
V	23	26.2±1.0	28.3±0.2	23.5	31.3	30.3	28.0	24.7
Cr	24	27.9±1.0	29.6±0.2	25.1	33.0	31.9	29.7	26.3
Mn	25	29.6±1.0	31.4±0.2	26.4	34.6	33.5	31.4	27.8

Here the energy shifts $K_{\alpha L^1}$ excitation by electron and photon is in agreement which means the energy shift of the satellite is independent of mode of excitation or projectiles. Among the theoretical estimation BS and B-HF values are called overestimated the shifts while HF is underestimated. And also SE is slightly underestimated. The excellent agreement with the analytic SCF calculations of Bhattacharya *et al*⁹.

Projectile Dependence of Intensity Ratio: Kawatsura²⁶ investigated projectile dependence and also chemical effects on X-ray satellites using *Be* and *BeO* targets. In the case of inner shell ionization for the *Be* atom is described by the direct coulomb excitation for light ion bombardment. For the *BeO* target, the spectra became more complicated. Both K_{α} diagram and K_{α}^2 hyper satellite lines became broader and shift to lower energy and then new satellite lines appear in higher energy side of each main peak. The ratio of intensities for low energy components of the satellite groups to those of high energy components increase with increasing projectile Z ²⁷. In the case of the KL^2 and KL^3 satellite groups, the peaks under consideration are composed of lines from a number of different terms and one would expect preferential population to have a much smaller net effect. Difference in relative intensity ratio of KL^1 obtained by photon and electron excitation modes was reported.

Table 4. The property of intensity ratio related with two modes of excitation^{4, 28}

Element	Intensity ratio by photon excitation	Intensity ratio by electron excitation
<i>K</i>	2.61±0.13	3.90±0.2
<i>Ca</i>	2.31±0.12	3.36±0.17
<i>Sc</i>	1.80±0.09	2.78±0.13
<i>Ti</i>	1.66±0.08	2.20±0.11
<i>V</i>	1.54±0.08	1.80±0.09
<i>Cr</i>	1.36±0.07	1.37±0.07
<i>Mn</i>	1.07±0.05	1.10±0.05

From the Table 4, intensity observed by photon excitation is less than electron excitation. But we see that the difference goes on decrease as Z increase. These shows relative intensity of K X-ray satellite is found to

be dependent on the mode of excitation being higher for electron than photon excitation. Watson *et al*²⁹ studied how $K_{\alpha}L^n$ relative intensity varies with different projectiles in Al, Cl and K.

Table 5. Relative K_{α} X-ray satellite intensity for Al, Cl, and K using 1.7MeV/amu²⁹

Target	Projectile	No. of L shell vacancy							
		0	1	2	3	4	5	6	7
Al	H	0.858	0.142	—	—	—	—	—	—
	He	0.664	0.285	0.051	—	—	—	—	—
	C	0.068	0.215	0.366	0.239	0.090	0.023	—	—
	O	0.045	0.128	0.312	0.293	0.168	0.053	—	—
	He	0.680	0.320	—	—	—	—	—	—
Cl	C	0.053	0.229	0.363	0.256	0.094	0.005	—	—
	O	0.028	0.133	0.304	0.316	0.170	0.049	—	—
	He	0.765	0.235	—	—	—	—	—	—
K	C	0.074	0.307	0.353	0.208	0.058	—	—	—
	O	0.045	0.185	0.316	0.271	0.142	0.042	—	—
	He	0.680	0.320	—	—	—	—	—	—

They have shown that, X-ray satellite intensity (Table 5) depends on targets, projectiles, and number of L shell vacancies. Intensity under He projectile decrease as a number of vacancy increase; while directly correlated with atomic number. In the case of C and O projectile the value of intensity is not consistent when Z increases.

Chemical Effects: The influence of chemical bond²⁶ on the energy shifts and the relative intensities of X-ray satellites is an interesting aspect of the study of these satellites. The relative intensities are particularly more susceptible to the chemical environment than the energy shifts. In some previous studies³⁰ it was shown that the satellite relative intensities are higher in compound than in the elements.

A noticeable chemical effect was observed in the case fluorine K. Ram Narayana *et al*¹¹. When $K_{\alpha}L^1$ relative intensity was measured in five fluorine compounds, on anomalous reduction of this relative intensity was observed in the case of potassium fluoride and strontium fluoride. This is attracted to phenomena called resonance electron transfer.

It can be seen that $K_{\alpha}L^1$ line relative intensity with respect to that of K_{α} diagram line is very much lower in the case of KF and SrF₂ compared to other compounds. This anomalously low value of the relative intensity was observed in these compounds in the study of Watson *et al*³¹ by ion excitation. The anomalous decrease in intensity of this satellite line in these compounds is explained as being due to the 'resonance electron transfer phenomena' proposed by Watson. In these phenomena electrons will be transferred from the outer *np* level of neighboring metal ion to the 2p level of fluorine ions which have been excited to 1s⁻¹ 2p⁻¹ states by the impact of photons. In the ground state, 2p level of the fluorine atom is confined to a narrow valance band. Impact of photons causes simultaneous ionization of 1s and 2p orbital's and these results in an increase in the 2p binding energy. Thus the 2p level of the fluorine atom is brought from the valance band to a level in close proximity with the outer *np* levels of the metal ion. When the energy difference between the outer *np* levels of the metal ions and the excited level of 2p vacancy of the fluorine ion in a fluorine compound becomes small enough, electron transfer from the metal ion to the ligand fluorine atom can take place thus filling up the 2p vacancy in the fluorine atom. In such a situation the spectator vacancy, necessary for the emission of a satellite line, disappear and consequently a diagram line is emitted in its place. This results in reduction in the intensity of the satellite line and enhancement of the intensity of the diagram line, thus giving a lower $K_{\alpha}L^1$ relative intensity ratio.

Z Systematics ↔ Z Dependence of Relative intensities: Sattar *et al*¹² measured energies and relative intensities of $K_{\alpha 3}$ and $K_{\alpha 4}$ X-ray satellites of sulphur and some sulphides by photon excitation. He compiled the experimental values of other elements in the Z range 11-17 and plotted $K_{\alpha 4}/K_{\alpha 3}$ intensity ratio as a function of Z. It can be seen that as Z increases from 11, $K_{\alpha 4}/K_{\alpha 3}$ intensity ratio first decreases up to Z= 14 and then increases sharply as it approaches Z=18. Therefore it was hypothesized that this ratio increases as the inert gas i.e., stable configuration is reached. To confirm this there was a need to measure this intensity ratio in Ne (Z=10) and Ar (Z=18).

Z Dependence of Energy Shift: Raju *et al*¹⁹ supplemented their data with those reported by other authors on K_{α} hyper satellite energy shift relative to the K_{α} diagram line in the Z range 12-30 and studied the variation of this with respect to Z. They found the relationship to be linear. They obtained from the plot of this $\Delta(E)$ versus Z, the following empirical relationship

$$\Delta E(K_{\alpha}^h) = -3.0 + 10.048Z$$

They also analyzed variation energy shift of $K_{\beta}L^1$ satellite relative to K_{β} diagram line as a function of Z and found the relationship to be linear. They compared these values with the theoretical values calculated using the formula of Burch *et al*⁸,

$$\Delta E(K_{\beta}L^1) = 18.541 + 2.304(Z - 6.828)$$

Where, σ is Slater's screening constant for L shell originally taken to be 4.15; the shift thus calculated was much lower than the experimental values. Using¹⁵ $\sigma = 6.828$, in the computation of this energy shift resulted in much improvement in agreement with theoretical values, but still the energy shift is overestimated.

4. CONCLUSIONS

WDXRF spectrometry is a crucial instrument for determining the energy shift and intensity of x-ray satellites because the instrument have eight different analyzing crystals and also other basic components like collimators. Due to this instrument the production of a satellites have been registered for a single-vacancy states existing in the shells is called X-ray satellites by critical consideration of self- absorption in the sample, crystal reflectivity, window absorption and efficiency of the detector.

From the basic theoretical investigations, the energy shift calculated by SCF approach was in better agreement with energy shift by electron excitation. From different mode of excitation; the energy shift by photon was less than by electron excitation for the same element. And also the relative intensities were particularly more susceptible to the chemical environment than the energy shift.

Generally, a review of the literature on X-ray satellites shows that, so far the research on these aspects is carried out on elements up to the atomic number 32. Beyond this as the wavelength of the satellites become smaller and smaller, crystals of matching 2d are to be used; this poses a challenge. Also, very few studies are found in literature on L X-ray satellites and hyper satellites. These studies can be extended to cover them. Because a number of synchrotron facilities are being developed throughout the world; using these tunable hard X-ray sources, energy dependence of these processes can be studied more efficiently. Finally, I believe that all these studies help to improve further knowledge on inner shell ionization processes.

5. REFERENCES

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