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The X-ray fluorescence cross-section for bromide and iodide compounds

A. Küçükönder[a]

Kahramanmaraş Sütçü İmam University, Faculty of Art and Sciences, Department of Physics, 46100 Kahramanmaraş, Turkey

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Abstract. The K_α and K_β X-ray fluorescence cross-sections for the bromide and the iodide compounds were measured by a high-resolution Si(Li) X-ray detector. The vacancies were produced by heavily filtered ^{241}Am gamma rays. We found that K_α and K_β X-ray fluorescence cross-sections are changed by chemical effect for different Br and I compounds. Experimental results were compared with the calculated values of Br and I elements.

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1 Introduction

X-ray fluorescence cross-section is an important parameter in atomic, molecular and radiation physics investigations and elemental analysis. In addition, comparison of measured X-ray fluorescence cross-sections with theoretical estimates provides a check on the validity of various physical parameters such as photo-ionisation cross-section, fluorescence yield, jump ratio and X-ray intensity ratios.

Earlier experimental K X-ray fluorescence cross-sections were measured using various excitation sources for different elements [1–13]. Büyükkasap [14] investigated K X-ray fluorescence cross-section in Cr and Ni alloys. Krause *et al.* [15] have calculated theoretically K_α and K_β X-ray fluorescence cross-sections. K X-ray fluorescence cross-sections of Cl, Br and I have been studied experimentally by some workers [1,5,8,13]. In these studies, it was assumed that Cl, Br and I were in elemental form. The results found in these experiments were compared with theoretical atomic values. However, Cl, Br and I are halogens and they normally occur in compound form in the nature. In compounds, we observed the existence of chemical effects on K X-ray intensity ratio. These effects are interpreted in terms of valence electron distribution and chemical bonding [16]. Although chemical effects on K X-ray intensity ratios have been studied by some workers, there are not any studies addressing chemical effects on K X-ray fluorescence cross-section. This is the first analytical investigation of K X-ray fluorescence cross-section on chemical effects.

In present study, K X-ray fluorescence cross-section for Br and I compounds were investigated.

2 Experimental

Experimental measurements were carried out on K characteristic radiations stimulated by 59.5 keV γ-photons of 75 mCi ^{241}Am source for Br and I compounds. The purity of commercially obtained materials was better than 99%. All the samples were sieved using 400 Mesh-powder samples of $(34 \times 10^{-3})\ \mathrm{g\,cm^{-2}}$ thickness and they were placed on a home built cylindrical sample holder supported by a mylar film. The experimental geometry is shown in Figure 1. As shown in Figure 1, the L X-rays from the lead shields were hold by Cu shield in order prevent them reaching the detector. X-rays emitted from the samples were detected with a Si(Li) detector (FWHM = 155 eV at 5.9 keV).

Two typical K X-ray spectra obtained from $\mathrm{I_2}$ and $\mathrm{Hg_2I_2}$ are given in Figure 2 for comparative purposes. The background was measured using the mean of a ten-channel approximation. Then the net peak area was obtained by the subtraction of the background from the total peak area.

3 Data analysis

The theoretical K_α and K_β X-ray fluorescence cross-sections have been calculated using the following relations:

$$\sigma_{K\alpha} = \sigma_{K(E)}\omega_K f_{K\alpha} \tag{1}$$

$$\sigma_{K\beta} = \sigma_{K(E)}\omega_K f_{K\beta} \tag{2}$$

where $\sigma_{K(E)}$ is the K shell photoionisation cross-section [17] for a given element at excitation energy E, ω_K is the fluorescence yields of the K shell line [18] and

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[a] e-mail: `a_kucukonder@hotmail.com`

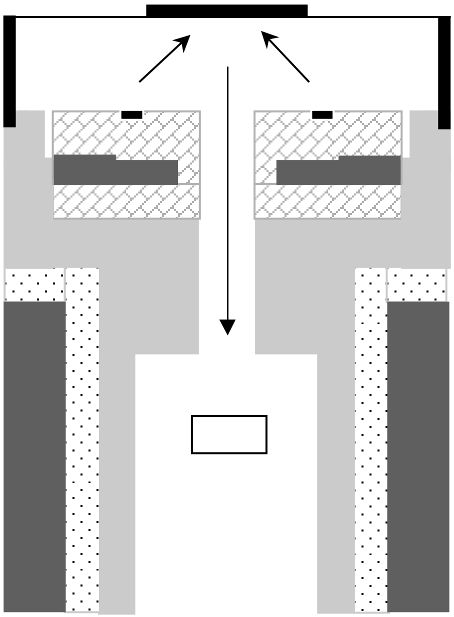

Fig. 1. Experimental geometry.

$f_{K\alpha}$ and $f_{K\beta}$ are the fractional ratio of the K_α and K_β X-rays.

$$f_{K\alpha} = \left[1 + \frac{I_{K\beta}}{I_{K\alpha}}\right]^{-1} \tag{3}$$

$$f_{K\beta} = 1 - f_{K\alpha} \tag{4}$$

where $I_{K\beta}/I_{K\alpha}$ is the K_β/K_α intensity ratio of K_β and K_α lines. In the present calculations, the value of $f_{K\alpha}$ was taken from *N*. Broll's values [18]. Experimental K_α and K_β X-ray fluorescence cross-sections (in $\mathrm{cm^2\,g^{-1}}$) were measured using the equation

$$\sigma_{Ki} = \frac{N_{Ki}}{I_o G \varepsilon_{Ki} T_\mathrm{t} t} \tag{5}$$

where N_{Ki} $(i = \alpha, \beta)$ is the number of counts observed for K_i $(i = \alpha, \beta)$ X-ray line of element. ε_{Ki} is the detector efficiency for K_i X-rays, I_0 is the intensity of exciting radiation, G is the geometrical factor, t is the mass of the sample in $\mathrm{g\,cm^{-2}}$ and T_t is the self-absorption correction factor of the target material. The self-absorption correction factor has been calculated by using the following expression:

$$T_\mathrm{t} = \frac{1 - \exp\left[(-1)\left(\frac{\mu_{(\mathrm{inc})}}{\cos\phi_1} + \frac{\mu_{(\mathrm{emt})}}{\cos\phi_2}\right)t\right]}{\left(\frac{\mu_{(\mathrm{inc})}}{\cos\phi_1} + \frac{\mu_{(\mathrm{emt})}}{\cos\phi_2}\right)t} \tag{6}$$

where ϕ_1 and ϕ_2 are the angles made by the radiation coming from the source and X-rays emitted along the normal of the sample surface respectively. This expression was obtained by assuming the incidence angle of the fluorescent X-rays subtended by the detector (ϕ_2) to be approximately 90°.

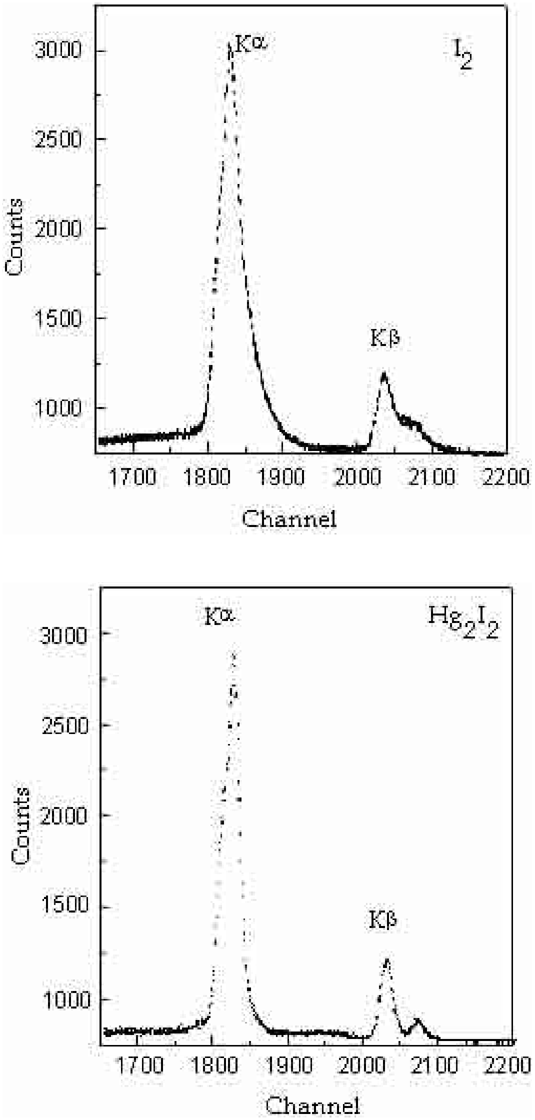

Fig. 2. Characteristic K X-ray emission spectra of I_2 and Hg_2I_2.

$\mu_{(\mathrm{inc})}$ $(\mathrm{cm^2\,g^{-1}})$ and $\mu_{(\mathrm{emt})}$ $(\mathrm{cm^2\,g^{-1}})$ are mass absorption coefficients [20] at the incident photon energy and fluorescent X-ray energy of sample respectively, t $(\mathrm{g\,cm^{-2}})$ is the measured thickness of sample. $I_0 G \varepsilon_{Ki}$ values in the present experimental set-up were determined in a separate experiment. Targets of pure elements with atomic number $30 \le Z \le 58$ emitting fluorescent radiation in energy range 8.5–40 keV were irradiated in same geometry and fluorescent radiation were counted. $I_0 G \varepsilon_{Ki}$ values for the present set-up were determined by the following relationship

$$I_0 G \varepsilon_{Ki} = \frac{N_{Ki}}{\sigma_{Ki} T_\mathrm{t} t} \tag{7}$$

where N_{Ki} is the number of counts under the K_α or K_β peaks.

Table 1. K X-ray cross-sections (barns atom^{-1}).

	$\sigma_{K\alpha}$		$\sigma_{K\beta}$		
Compounds	Experimental*	Calculated	Experimental*	Calculated	Interatomic distances (A^0)
Br	——	153.05	——	22.87	
Br_2	——	——	——	——	2.29
$C_{21}H_{16}Br_2O_5S$	77.94 ± 7		13.01 ± 0.9		
$HgBr_2$	——		15.11 ± 1.0		2.48
$C_7H_5O_2Br$	102.80 ± 6		16.30 ± 1.0		
$KBrO_3$	128.30 ± 6		21.33 ± 1.2		2.94
C_6H_6BrN	137.71 ± 5		22.20 ± 1.1		
$C_{19}H_{10}Br_4S$	139.20 ± 5		22.50 ± 1.3		
KBr	174.01 ± 5		28.26 ± 1.4		3.30
NaBr	189.17 ± 7		30.68 ± 1.5		2.98
NH_4Br	213.43 ± 8		35.81 ± 2.0		
I	——	956.36	——	208.51	
NH_4I	919.30 ± 55		200.17 ± 12.0		
I_2	965.10 ± 62		208.80 ± 12.4		2.66
$NaIO_3$	1016.80 ± 64		217.23 ± 15.1		3.16
KI	1082.90 ± 55		218.70 ± 14.2		3.53
Hg_2I_2	1076.50 ± 68		221.00 ± 16.8		
KIO_3	1095.80 ± 59		216.80 ± 16.9		

* σ(barns/atom)= σ(cm^2 g^{-1})/0.007537 for Br (Ref. [21]), σ(barns/atom)= σ(cm^2 g^{-1})/0.004746 for I (Ref. [21]).

4 Results and discussion

The experimental values of K_α and K_β X-ray fluorescence cross-sections in Br and I compounds are given in Table 1. The average errors in present measurements are as follows: 2% due to $I_0 G \varepsilon$ determination, 2% due to counting statistic (for the K_α and K_β X-ray peaks is 0.7–2.8%), 2% due to target thickness measurements and 2% for self absorption correction. K_α and K_β fluorescence cross-sections measured for Br and I compounds were compared with calculated values for Br and I. The results obtained for Br and I compounds could not be compared with literature since there are no experimental or theoretical values present. It is a well-known fact that orbital energy levels of L, M, N and O shells get closer to each other with increasing quantum number n and outer energy levels become sensitive to the chemical environment by this effect. Thus, outer energy levels are more strongly affected by ligands according to crystal field theory. In addition to this, valence electrons participating in the formation of a chemical bond are removed from the atom and this causes a change in the electronic screening and a change in the outer shell binding energies. These effects play an important role in the K_α and K_β X-ray transitions. Br and I are halogens and, in nature, they normally occur in compound form. Since Br has an unfilled 4p shell, and I has an unfilled 5p shell, they are sensitive to these effects. Electron affinities and electronegativities of the halogens (Br and I) are larger than those of other elements. According to the results shown in Table 1, K X-ray cross-sections of Br and I compounds depend on chemical structure. As seen from Table 1, Br and I molecules have different interatomic bond distances between ligands and central atom. Different interatomic bond distances cause different interaction between ligands and central atoms. K X-ray transitions may be affected by these interactions. An increase in K X-ray cross-sections are observed with increasing interatomic distances. This is probably due to the increase in binding energies of outer shell electrons. According to Molecular Orbital Theory, molecular orbitals get closer to nucleus by increasing interatomic distances. That is, binding energies of outer shell electrons in molecules are higher than that of free atoms. This state causes a decrease in Auger effect and an increase in fluorescent X-rays. Thus, K_α and K_β fluorescence cross-sections change with increasing interatomic distances. Chemical bonding type (ionic, metallic, covalent) affects the K X-ray fluorescence cross-sections. The individual characteristics of the structure of molecules, complexes and crystals (polarity valency and electronegativity of atoms, coordination number, ionic character of the covalent bond, etc.) mainly affect the K X-ray fluorescence cross-sections. A change in chemical bond leads a change in its valence electron density. The electron density decreases or increases depending on type of bonding with adjacent atoms in molecule or crystal. The overlap of the electronic distribution of the neighbouring atoms is also of importance. However, this effect depends upon various factors such as the number of first neighbouring atoms, the type of bonding and electronegativity.

Chemical effects on the K X-ray cross-sections for Br compounds are larger than I compounds because the ionic character of I compounds is less than that of Br compounds. A significant difference appears to exist between the experimental and theoretical $\sigma_{K\alpha}$ and $\sigma_{K\beta}$ values of Br and I. The reason for this is that the theoretical calculations of I and Br were carried out in element form.

Consequently, it is clear from the table that the K X-ray cross-sections of Br and I compounds depend on chemical structure.

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