

X-Ray L_{III} Absorption Edges of Bismuth Halides*

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The position of the bismuth L_{III} absorption discontinuity has been studied in pure bismuth metal and in its halides, BiF_3 , $BiCl_3$, $BiBr_3$ and BiI_3 using a focussing spectrograph of the transmission (Cauchois) type. In all these compounds the discontinuity is found to shift towards the high energy side with respect to that in the pure metal. The experimental material presented in this study convincingly shows that the position of the L_{III} absorption edge is determined by the partial charge of the absorbing atom and not by its valence.

Introduction

Several workers [1–8] have studied the X-ray absorption edges of metal ions in their compounds and have reported a change in wavelength of the absorption edge. The range of parameters affecting the edge position (e.g. electronegativity, interatomic distance, crystal structure, covalent electrons, the valence states of the atom, etc.) is so wide that a generally valid theory for chemical shifts does not exist. However, it is obvious that it is the electronic structure of the atom that determines the interatomic bonding. The chemical shifts in X-ray absorption spectra, therefore, present a possible method of characterizing the bonding.

In principle, the change in the absorption edge position (i.e., the chemical shift) should depend on the energies of both the outer and inner levels involved in the electronic transition. However, this change is likely to reflect primarily the character of the outer level since the inner level shift is generally small. For electron acceptors (or anions) these absorption shifts are generally towards the low energy side, and vice versa for electron donors (or cations), with a few exceptions. If the atoms have different electronegativities, the bond becomes partially ionic. The atom of initially higher electronegativity is expected to acquire more than an equal share of the valence electrons. In this communication, we present some of the results of our X-ray spectroscopic investigations on bismuth compounds and attempt to correlate these results with the partial charges.

Experimental Details

The spectra were recorded on Kodak X-ray photographic films using a 40 cm Cauchois-type bent crystal spectrograph. The $(\bar{2}01)$ planes of a well tested mica crystal were used as reflecting planes, giving a dispersion of about 12.3 X. U./mm on the films. A Phillips sealed X-ray tube with a molybdenum target operated at 25 kV and 15 mA was employed as the source of white radiation.

In this investigation we have used spec-pure bismuth metal and the compounds supplied by Johnson Matthey and Co., London. The absorbing screens were prepared by pressing uniformly the fine powder of the samples between two cellophane tapes fixed on an aluminium frame. The optimum thickness of the absorber and the exposure time for each sample were determined after many trials. Microphotometer records of the spectra were obtained with a magnification X 50 on the Moll microphotometer. The errors in the measurement, as obtained statistically, lie within ± 0.5 eV. Other experimental details are described elsewhere [9].

Results

The shape of the L_{III} discontinuity of Bi is found to be fairly simple, more or less of the arctangent type, for pure bismuth as well as for the compounds studied. Therefore, the measurements of the wavelengths of the absorption discontinuities were made on the inflection points of the L_{III} edges according to the usual procedure [10].

The results of our measurements on the position of L_{III} discontinuity of bismuth in the pure metal and its compounds are given in Table 1. The observed value of the wavelength for the metal is in good agreement with that given by Sandström [10]. It can be seen that the absorption edge shifts towards the high energy side in all the compounds

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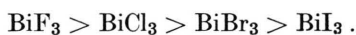


Table 1. Data on bismuth L_{III} absorption discontinuity.

Ab-sor-ber	Wave-length $\lambda(\text{\AA.U.})$	Energy E $\pm 0.5 \text{ eV}$	Chemical shift ΔE (eV)	Va- lency	Electro- negativity difference*
Bi	921.47	13,426.83	—	3	—
BiF ₃	920.99	13,433.82	6.99	3	2.59
BiCl ₃	921.15	13,431.49	4.66	3	1.77
BiBr ₃	921.33	13,428.87	2.04	3	1.37
BiI ₃	921.34	13,428.72	1.89	3	0.68

* R. T. Sanderson, Inorganic Chemistry, Reinhold Company, New York 1967, p. 80.

with respect to its position in the metal. The magnitude of the chemical shift is in the sequence



Discussion

(i) Chemical Shift and Valency of the Metal Ion

The shift of the X-ray absorption edge due to chemical combination first observed by Bergengren [11] and later, by others [1, 12–14] has been found to depend primarily on the valency of the element in question. Kunzl [14] made a critical examination of the experimental work concerning the displacements of the K absorption discontinuities of atoms in different oxidation states. Kunzl's law, according to which the edge shifts are governed by the valency, has been recently shown [15] to hold only qualitatively for cationic shifts in compounds. One observers either a positive or a negative shift depending upon whether the absorption ion is a cation or an anion. A glance at Table 1 shows that the chemical shifts are not governed by the valency, at least not in a direct manner. Had Kunzl's law been applicable to the system we have studied, all the positive shifts would be of the same magnitude. In this respect our study gives support to the X-ray spectroscopic studies of Sapre and Mande [15] on gallium, germanium and arsenic compounds.

(ii) Chemical Shift and Charge Transfer

The outer electronic configuration of the bismuth atom is $6s^2 6p^3$ and that of halide atoms is $ns^2 np^5$ ($n = 2, 3, 4, 5$). Sarode and Chetal [16] have shown that in a compound the absorption edge of an atom shifts towards the high or low energy side relative to its position in the pure element, depending upon whether the absorbing ion donates or accepts electrons from the other atom of the

compound. In the case of the compounds studied in this investigation, the L_{III} edge shifts, which are towards the high energy side, suggest that an electron transfer takes place from bismuth to the halide atoms, i.e. the bismuth ion plays the role of a cation in the bismuth halides. The electrons that are transferred are the outer, loosely bound electrons (perhaps 6p valence electrons). That Bi ion behaves as a cation in the bismuth halides is corroborated by the electronegativity criterion [17, 18]. Our results, in this regard, give support to the bonding scheme of Mooser and Pearson [19] for BiI₃, in which the three 6p electrons of bismuth are transferred to fill the anion orbitals.

(iii) Chemical Shift and Covalent Character of the Bond

In the last column of Table 1 electronegativity differences are given, using the electronegativity scale devised by Sanderson [18]* between the two constituent atoms of the bismuth compounds. It can be seen that the greater the chemical shift, the greater is the electronegativity difference and consequently the smaller is the covalent character of the bond. The chemical shift, thus, gives an idea of the covalent character of the bonds.

It may be mentioned here that Debies and Rabalais [20] who have studied the X-ray photoelectron spectra of Bi₂O₃, Bi₂S₃, Bi₂Se₃ and Bi₂Te₃ found that the bismuth core levels (viz. $5d_{5/2}$, $5d_{3/2}$, $5p_{3/2}$, $5p_{1/2}$, etc.) shift to higher ionization energy with increasing electronegativity of the group VI element (Te, Se, S, O) in these compounds.

We remark here that the charge density distribution plot for the valence electrons in BiI₃ has been obtained by Schlüter et al. [21, 22] employing the EPM (Empirical Pseudopotential Model) method. The charge distribution around the anions in BiI₃ was found to be less spherically symmetric, indicating the presence of greater covalent character in the bonding.

(iv) Chemical Shift and Partial Charge

The X-ray absorption spectra determine the difference between the energies of initial and final states. Therefore, in a one electron picture [23],

* Electronegativity (SR), according to Sanderson [18], is the ratio of the average electron density of an atom to that of a hypothetical, isoelectronic inert atom. (The latter value is obtained by interpolation between the values for the respective inert gases.)

the shifts of both the core level and the outer level are involved. The initial state involved in the absorption processes for the bismuth halides studied is the L_{III}(2p_{3/2}) level having p-symmetry, while the final state is of d (or s) symmetry. The X-ray photoelectron spectroscopic data on 2p_{3/2} core level shifts of bismuth ion in halides being unavailable, it is difficult to make any meaningful estimates of the absorption shifts for our compounds. However, since several workers [24–28] have in fact observed appreciable core level shifts in a related set of group VA compounds it is perhaps appropriate to begin with the assumption that the core level shifts of bismuth ions in halides are non-zero and that the chemical shifts are due to the shifts of both the outer and inner levels.

We now try to see if there exists a correlation between these absorption shifts and the partial charges on the absorbing atoms (Bi).

The determination of the charge distribution presents a difficult problem since it is not easy to visualize just what is meant by charge distribution, and more so, to evaluate it quantitatively in terms of charge per atom. An approximate solution of this problem can be approached by a study of the electronic adjustments that occur with the formation of chemical bonds. This approach, although far from rigorous, leads to partial charges in reasonable accord with other approaches, e.g. dipole moments. Various theoretical methods [29–32] have been proposed to evaluate this charge. Numerous experimental methods [33–34] have also been developed to determine charges in compounds. However, it has been pointed out [34] that the values of charges obtained by different methods cannot always be compared due to different physical arguments inherent in them. Sanderson [18] has proposed a method for the evaluation of partial charges in compounds. This method, which is based on the principle of electronegativity equalization*, is inherently simple and straightforward, and permits the calculation of partial charges in all type of binary as well as complex compounds, and has earlier been successfully used in X-ray photoelectron

spectroscopic (XPS) work of Seals et al. [35] on zinc, cadmium and mercury compounds. According to Sanderson [18], the partial charge on an atom of a molecule or ion can be defined as the ratio of the electronegativity change produced by the atoms combining with other atoms, to the electronegativity change that would result from acquisition of unit charge. Mathematically,

$$\delta_E = \frac{SR_M - SR_E}{(SR_E - E^{n+})/n}, \quad (1)$$

where SR_M is the stability ratio or electronegativity of the molecule (or ion) and is the geometric mean of the electronegativities of all the atoms before combining, SR_E is the electronegativity of the free element E whose partial charge δ_E in the molecule is to be determined, n being the valence of the atom under consideration, $(SR_E - E^{n+})/n$ is the electronegativity change per unit charge. Sanderson has calculated this quantity to be equal to $2.08/\sqrt{SR_E}$. The values of SR_E , SR_E' (electronegativity of halide atom), SR_M , δ_E , δ_E' (partial charge on halide atom), $2.08/\sqrt{SR_E}$, taken from reference [18], are given in Table 2. The charge is in units of electronic charge (4.8×10^{-10} e.s.u. per electron).

Tables 1 and 2 show that the magnitude of the shift varies directly as the charge on the bismuth ion, indicating the same trend of the covalent character of the bond between the bismuth and halide atoms, as discussed in Section (iii).

We have plotted the chemical shift ΔE for the L_{III} absorption discontinuity of bismuth against the partial charge δ_E on bismuth ion in Figure 1. It is seen that all the points within experimental

Table 2. Data employed for calculating the values of partial charges.

Compounds	Electro-negativity SR_E	Electro-negativity SR_E'	Electro-negativity SR_M	Partial charge δ_E	Partial charge δ_E'
BiF ₃	3.16	5.75	4.951	+ 0.50	– 0.16
BiCl ₃	3.16	4.93	4.412	+ 0.34	– 0.11
BiBr ₃	3.16	4.53	4.140	+ 0.26	– 0.09
BiI ₃	3.16	3.84	3.658	+ 0.13	– 0.04

$2.08/\sqrt{SR_E}$ values for Bi, F, Cl, Br, I, are 3.702, 4.988, 4.618, 4.426 and 4.077, respectively.

SR_E = Electronegativity of element E (Bi),

SR_E' = Electronegativity of element E (F, Cl, Br, I),

SR_M = Electronegativity of compound,

δ_E = Partial charge on Bi ion,

δ_E' = Partial charge on halide ion (F, Cl, Br, I).

* The principle of electronegativity equalization may be stated: When two or more atoms initially different in electronegativity combine chemically, they become adjusted to an equal intermediate electronegativity in the compound. To determine this intermediate value, it is necessary to assume some basis for estimation. The geometric mean of the electronegativities of the atoms involved in the compound seems superior.

errors lie on a straight line except in the case of BiBr₃, where the deviation is more pronounced. We are unable to give an explanation for this discrepancy. The linear plot of ΔE versus δ_E should pass through the origin, since the ΔE values are obtained with reference to the position of the discontinuity in the metal in which there is no effective charge transfer from one atom to another. We find on extrapolation that this is indeed the case, i.e.

$$\Delta E = m \delta_E \quad (\text{where } m = 13.86). \quad (2)$$

The plot shown in Fig. 1 is similar in nature to the curve obtained earlier by Batsanov et al. [36–38] for the manganese K absorption edge shifts in its compounds and for the neodymium L_{III}, praseodymium L_{III} and cerium L_{III} absorption edge shifts in their compounds. However, it differs somewhat from that obtained by Sapre and Mande [15] for the compounds of germanium, gallium, arsenic and selenium, who observed some sort of saturation in the effective charge (q), beyond $q > 1.3$. However,

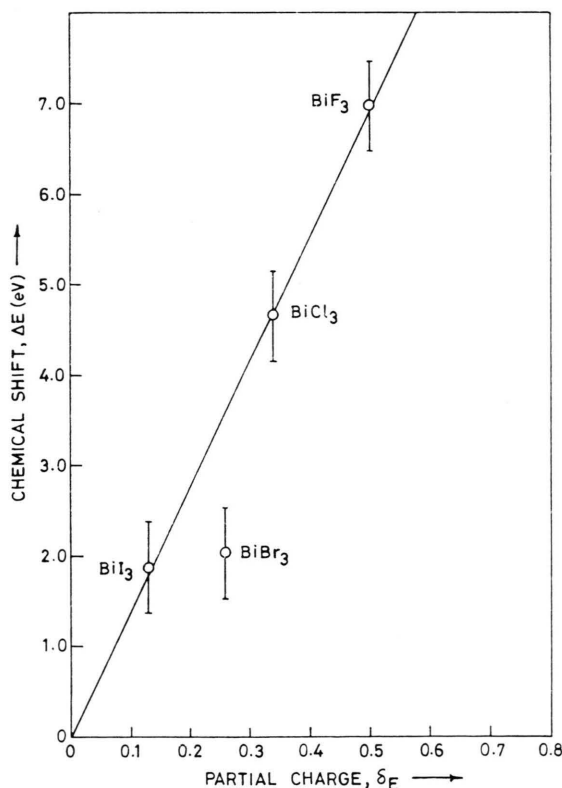


Fig. 1. Plot showing the dependence of the chemical shift ΔE on the partial charge δ_E for bismuth halides.

the curve of these authors can be considered to be linear for compounds in which the charge q is smaller than 1.3 electrons per atom. Although it is likely that this range of linearity may vary from element to element, we note that the partial charge values in all the compounds studied in the present investigation are smaller than 1.3. An important difference may be that we have used Sanderson's method [18] to calculate the charges while Sapre and Mande used Suchet's model [32].

We may mention here that in cases where the calculation of the partial charge is not possible for some reason, the ΔE vs. δ_E curve may provide some information regarding the nature of the bonding.

Finally, it would be interesting to compare the conclusions drawn from our X-ray spectroscopic measurements with those obtained from X-ray photoelectron spectroscopic (XPS) data, but unfortunately, the XPS data on core levels, viz. 2 P_{3/2} levels (the initial level involved in our spectra), are not available for the bismuth halides, except some other core levels data on BiF₃ and BiI₃. Kowalczyk et al. [39] in their X-ray photoemission study of the total valence band density of states of BiI₃ have studied the binding energies of the 5d_{3/2} and 5d_{5/2} levels of bismuth in BiI₃. Since the chemical shifts of these levels relative to the levels of pure bismuth have not measured, we find it difficult to compare our results with theirs. Morgan et al. [28, 40–41] have studied the binding energies of 4f_{5/2} and 4f_{7/2} levels of bismuth in pure bismuth, BiF₃, BiI₃ and other bismuth compounds by X-ray photoelectron spectroscopic technique. The 4f_{7/2} level shifts for BiI₃ and BiF₃ are 2.4 and 3.9 eV while the 4f_{5/2} shifts are 2.4 and 3.8 eV, respectively. This shows the expected general increase in binding energy shift with increasing substituent electronegativity (and hence decreasing covalent character). This is in accord with our conclusion drawn from our X-ray spectroscopic study.

Conclusion

From the results of the X-ray spectroscopic investigation of the bismuth halides in combination with the results of our earlier investigations [42], the following conclusions can be drawn:

(1) the chemical valence of an element does not seem to determine directly the position of the X-ray

absorption edge in a compound, indicating non-adherence to Kunzl's law;

(2) the absorption edge in a compound shifts towards the higher or lower energy side with respect to that in the pure element depending upon whether the charge on the absorbing ion is positive or negative. Thus, the chemical shifts may be used to distinguish between cations and anions in compounds in cases of ambuity and

(3) the magnitude of the chemical shifts, positive for a cation and negative for an anion, seems to be primarily determined by the partial charge on the absorbing ion.

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