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An X-Ray Emission Spectroscopic Investigation of the Chemical Bond of Sulfur. I. The Peak Shift of $K\alpha$ and the Number of Valence Electrons of the Sulfur Atom in Compounds

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The energy shifts of the S$K\alpha$ doublet have been measured in fifty sulfur compounds in solid or liquid states, using rhombic sulfur as a standard. The values were the same as those obtained by Faessler and Goehring, although a slight discrepancy was observed on sulfites and sulfates. The mean number of the valence electrons, N, associated with the sulfur atom in compounds has then been calculated from the shifts according to a theoretical correlation presented by Coulson and Zauli. The values of N have been found to be 6.7, 6.3, 5.2, 4.7, 4.7, and 4.3 for inorganic sulfides, organic sulfides, sulfoxides, sulfites, sulfones and sulfates respectively, assuming that $N=6.0$ for rhombic sulfur. The dipole moments evaluated from the values of N and structural data were 4.9, 4.8 and 5.2D, for dimethyl sulfoxide, dimethyl sulfone and diphenyl sulfone, respectively; these values were almost compatible with the experimental values of 3.9, 4.41 and 5.14D. respectively.

It has been known that the wavelength,1,2) the relative intensity,3,4) and the peak shape5) of characteristic X-ray lines emitted by certain elements depend to some extent on the chemical bond or the valence state of the elements. A similar dependence has also been observed on a non-diagram X-ray line of an element, for example, the $K\alpha_{3,4}$ of magnesium.6)

In particular, Faessler *et al.*2) have investigated experimentally the $K\alpha$ doublet of sulfur in non-volatile compounds; they have pointed out that a correlation exists between the formal oxidation number of the atom and the energy shift of $K\alpha$ radiation. Recently, Coulson and Zauli7) have made a quantum-mechanical calculation of the same shift as a function of the number of the valence electrons in the outer-shell (3s and 3p electrons), and have successfully evaluated the mean number of valence electrons associated with a sulfur atom in inorganic and organic sulfides, thiopiperidine, sulfites, and sulfates from their experimental data. These works should be specially emphasized, since they suggest that X-ray emission measurement may be useful for the direct determination of the real charges localized on a atom in the bonding state. However, the reliability of the calculated values should be examined from both experimental and theoretical points of view, because of the small value of the shift and also because of the approximation used for calculating the energy of the $K\alpha$ transition.

The purpose of the present investigation is, first, to check experimentally the reliability of the correlation found by Faessler *et al.* and, second, to examine the propriety of the correlation presented by Coulson and Zauli. For this purpose, many more samples, including liquid samples as well as the solid samples hitherto examined, were measured.

Experimental

A standard Rigaku-Denki D-3F Fluorescent X-ray Spectrograph was specially modified for the present investigation as follows: 1) Attachments A and B, shown in Fig. 1, were attached; they made it possible to detect the $K\alpha$ line of sulfur at a high angle of about 144°30′ (2θ), using a sodium chloride analyzing crystal.

2) Two Soller slits, I and II, were inserted into the light path in order to attain a high resolution. Slit I was 10 cm long, with 0.08 mm spacing, while slit II was 5 cm long, with 0.10 mm spacing.

3) The X-ray tube, the sample holder, and the Soller slit I were carefully arranged so that the high resolution was obtained with a minimum loss of the X-ray intensity. The glacing angle, α, indicated in Fig. 1 was 15°.

A Machlett OEG-50S chromium target X-ray tube was operated at 40 kV, 40 mA. A gas-flow proportional counter and a pulse-height analyzer were used. The helium path was maintained using a flow of 1.5 *l*/

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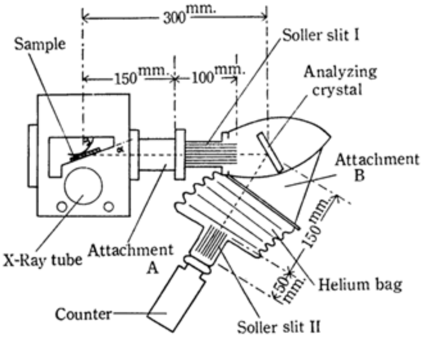

Fig. 1. Schematic diagram of X-ray analyzing system.

min. The room temperature was kept at 25±1°C. The X-ray intensity was counted for 1 min at an angle changed by 1.5′ (2θ) stages. The peak position of S$K\alpha$ was determined with an accuracy of 1′(0.0002Å) by referring it to the third-order reflection lines of Co$K\alpha_1$(5.36676 Å) and Co$K\alpha_2$(5.37834 Å). Cobalt oxide, used as a standard material, was not mixed with a sample during the measurements in order to avoid any error in the determination of the peak position due to the overlap of peaks.

Most of the sample materials were guaranteed reagents. α-Manganese sulfide containing lead sulfide as an impurity was prepared from a mineral. Zinc sulfide, nickel sulfide, cadmium sulfide, arsenic sulfide, and a mixture of β- and γ-manganese sulfide were prepared by the precipitation method, and confirmed to be pure by means of X-ray diffraction.

Solid samples were pulverized and then formed into tablets 4 cm in diameter under pressure before being measured, while liquid samples were held in a standard liquid sample holder with a Myler window.

It was verified by X-ray diffraction or infrared spectroscopy that the X-ray irradiation for sample excitation did not give rise to any change in the quality of the samples, although their temperatures were observed to rise up to a steady value of about 35°C after thirty minutes of X-ray irradiation.

Results and Discussion

Under our experimental conditions, we could not resolve the $K\alpha$ doublet of sulfur because of the insufficient resolution of the present equipment compared with that of Faessler *et al.* The values of the peak positions are given in Table 1. The peak position of the $K\alpha$ doublet is generally inconsistent with the position corresponding to the

TABLE 1-a. WAVELENGTH OF $K\alpha$ AND MEAN NUMBER OF VALENCE ELECTRONS OF SULFUR ATOM IN COMPOUNDS

Sample No.	Compound	Formal oxidation number	Wavelength Å	Energy eV	Mean number of valence electrons
I-1	As_2S_3	−2	5.3730	2307.4	6.7±0.5
2	Sb_2S_3	−2	31	7.4	6.7±0.5
3	NiS	−2	30	7.4	6.7±0.5
4	FeS	−2	31	7.4	6.7±0.5
5	CdS	−2	32	7.3	7.5±0.5
6	ZnS	−2	29	7.5	6.3±0.5
7	α-MnS	−2	30	7.4	6.7±0.5
8	β- and γ-MnS	−2	29	7.5	6.3±0.5
9	CaS	−2	30	7.4	6.7±0.5
10	$Na_2S\cdot 9H_2O$	−2	30	7.4	6.7±0.5
	Average	−2	30	7.4	6.7±0.5
II-a-1	S_8(rhombic)	0	5.3727	2307.6	(6.0)
II-b-6	NaSCN		5.3729	2307.5	6.3±0.5
7	KSCN		30	7.4	6.7±0.5
	Average		30	7.4	6.7±0.5
III-1	$CaSO_3$	+4	5.3710	2308.3	4.7±0.1
2	Na_2SO_3	+4	09	8.3	4.7±0.1
	Average	+4	10	8.3	4.7±0.1
IV-1	$ZnSO_4\cdot 7H_2O$	+6	5.3703	2308.6	4.3±0.1
2	$CaSO_4$	+6	03	8.6	4.3±0.1
3	Na_2SO_4	+6	00	8.7	4.2±0.1
4	K_2SO_4	+6	00	8.7	4.2±0.1
5	$(NH_4)_2SO_4$	+6	00	8.7	4.2±0.1
6	$N_2H_6SO_4$	+6	05	8.5	4.4±0.1
7	32N H_2SO_4	+6	03	8.6	4.3±0.1
7′	2N H_2SO_4	+6	02	8.6	4.3±0.1
	Average	+6	02	8.6	4.3±0.1

TABLE 1-b. WAVELENGTH OF $K\alpha$ AND MEAN NUMBER OF VALENCE ELECTRONS OF SULFUR ATOM IN COMPOUNDS

Sample No.	Compound		Wave-length Å	Energy eV	Mean number of valence electrons
II-a-2	Hexadecanethiol	$CH_3(CH_2)_{14}SH$	5.3725	2307.6	6.0±0.4
3	Sodium 1-thiol acetate	$NaOOCCH_2SH$	28	7.5	6.3±0.5
4	Toluene-4-thiol	$CH_3C_6H_4SH$	28	7.5	6.3±0.5
5	2-Thiol benzoic acid	$HOOCC_6H_4SH$	28	7.5	6.3±0.5
6	Di-(2-hydroxyethyl)sulfide	$(CH_2OHCH_2)_2S$	29	7.5	6.3±0.5
7	Dibutyl sulfide	$[CH_3(CH_2)_3]_2S$	29	7.5	6.3±0.5
8	Diphenyl sulfide	$(C_6H_5)_2S$	27	7.6	6.0±0.4
9	Di-*t*-butyl disulfide	$[(CH_3)_3C]_2S_2$	28	7.5	6.3±0.5
10	Dibenzyl disulfide	$(C_6H_5CH_2)_2S_2$	30	7.4	6.7±0.5
11	Carbon disulfide	CS_2	23	7.7	5.8±0.3
II-b-1	Thiourea	NH_2CSNH_2	5.3730	2307.4	6.7±0.5
2	Thiosemicarbazide	$NH_2CSNHNH_2$	29	7.5	6.3±0.5
3	1,3-Diphenyl-2-thiourea	$(C_6H_5NH)_2CS$	31	7.4	6.7±0.5
4	Allyl isothiocyanato	$CH_2{:}CHCH_2NCS$	27	7.6	6.0±0.4
5	Phenyl isothiocyanato	C_6H_5NCS	27	7.6	6.0±0.4
II-c-1	Thiophene	$CH{:}CHCH{:}CHS$	5.3727	2307.6	6.0±0.4
2	Thenoylic acid	$HOOCC{:}CHCH{:}CHS$	29	7.5	6.3±0.5
3	Benzo[*d*]thiazol	$C_6H_4\text{-}S\text{-}CH{:}N$	29	7.5	6.3±0.5
4	Phenothiazine	$C_6H_4\text{-}S\text{-}C_6H_4NH$	29	7.5	6.3±0.5
III-3	Dimethyl sulfoxide	CH_3SOCH_3	5.3718	2307.9	5.3±0.2
4	Sodium formaldehyde sulfoxylate	$CH_2OH\text{-}SO\text{-}ONa$	15	8.1	5.0±0.2
IV-8	Sulfamic acid	NH_3SO_3	5.3703	2308.6	4.3±0.1
9	Toluene-4-sulfonic acid	$CH_3C_6H_4SO_2OH$	07	8.4	4.6±0.1
10	Benzenesulfonyl amide	$C_6H_5SO_2NH_2$	08	8.4	4.6±0.1
11	Ethylbenzene-4-sulfonyl chloride	$C_2H_5C_6H_4SO_2Cl$	09	8.3	4.7±0.1
12	Diphenyl sulfone	$C_6H_5SO_2C_6H_5$	08	8.4	4.6±0.1
13	Dimethyl sulfone	$CH_3SO_2CH_3$	10	8.3	4.7±0.1

center of gravity of $K\alpha_1$ and $K\alpha_2$ on account of the asymmetry in shape of both the $K\alpha_1$ and $K\alpha_2$ lines. In spite of this difficulty, the relative shift of the $K\alpha$ doublet, in which we are interested, should be consistent with that of the $K\alpha_1$ or the $K\alpha_2$ line within the limits of experimental error, at least for inorganic sulfides, thiopiperidine, sulfites, and sulfates, since their doublet intervals have a constant value of 2.8 x. u.[2] As may be seen in Fig. 2, a discrepancy in the shift, especially in sulfites and sulfates, was observed between our data and Faessler's. This discrepancy may be assumed to be responsible for the results of Faessler *et al.*, where the use of cobalt as an internal standard material give rise to an apparently short wavelength shift in sulfites and sulfates, because the overlap of S$K\alpha_1$ with Co$K\alpha_1$III is much larger in sulfites and sulfates than in rhombic sulfur and sulfides.

The mean number of the valence electrons, N, was calculated from our data according to the equation presented by Coulson and Zauli:

$$\delta E = n(n+3)/8$$

where $n=6-N$, and where δE is the difference between the $K\alpha$ transition energy for any compound and that for rhombic sulfur.

It should be noticed, as is shown in the last column in Table 1, that the values for sulfides are essentially more inaccurate than those for sulfites and sulfates, because the change in the shift becomes smaller with the increase in the number of valence electrons.

It should also be noticed that the S$K\alpha$ radiation is associated with a sulfur atom with one inner-shell electron missing, but not with a normal atom. However, considering the experimental finding that the energy of the $K\alpha$ transition is equal to the difference in energy between the two corresponding absorption edges, with an accuracy of about 1 part in 10000 (*cf.* Ref. 1, pp. 182, 214),

TABLE 2. THE OBSERVED AND EVALUATED DIPOLE MOMENTS

Compound	Dipole moment, Debye		Interatomic distance S-O[11] Å	Bond angle of O-S-O[11] deg.
	Obs.	Calc.		
$(CH_3)_2SO$	3.9	4.9±1.4	1.47	—
$(CH_3)_2SO_2$	4.41	4.8±0.7	1.43	115*
$(C_6H_5)_2SO_2$	5.14	5.2±0.7	1.43*	115*

* The values were assumed to be the same as for dimethyl sulfone.

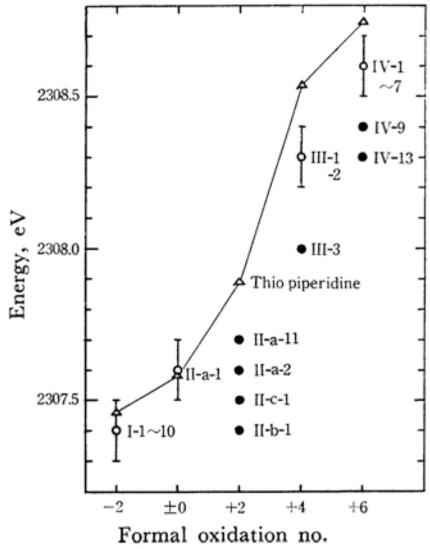

Fig. 2. Dependence of the energy shift of $SK\alpha$ on the formal oxidation number.
● and ○: observed values
△ : Faessler's values

the effect of this electron missing on the energy shift of $K\alpha$ may be largely ignored. The following discussion is, therefore, based on the assumption that the calculated values refer to a normal sulfur atom.

The values in Table 1 are, on the whole, reasonable; in the organic sulfides (Sample No. II), which may have two single bonds or one double bond, we find that the sulfur atom is almost neutral, although the values scatter with the variety of the compounds. It may also be reasonable that the number of valence electrons for all sulfones except sulfamic acid is larger than that of sulfates, since sulfones are sulfate derivatives, where one or two oxygen atoms of sulfate are replaced by one or two less electronegative atoms than the oxygen atom, and hence electrons localized in the sulfur atom may increase more in sulfones than in sulfates. It may be said that sulfamic acid is the most sulfate-like molecule of the sulfones examines here form the point of view of the electronegativity scale of Pauling.[8] The situation is the same for sulfoxides in the sense that the sulfur atom in sulfoxides should be more neutral than that in sulfites.

A more direct criterion for the theory may be obtained by comparing the dipole moment observed with that calculated from the data in Table 1 after having made suitable assumptions. The moment of dimethyl sulfoxide may safely assumed be attributed to the S-O bond, because alkyl sulfoxides of the R-SO-R (R$=CH_3$, C_2H_5, iso-C_4H_9, $C_6H_5CH_2$) type have a moment with the almost constant value of 3.9D.[9,10] and the ionic character of the S-C bond is negligible.[8] Likewise, the moments of dimethyl sulfone and diphenyl sulfone may be due to the two equivalent S-O bonds; hence, they will be $2r_{S-O}q_O\cos(\theta/2)$, where r_{S-O} is the interatomic distance of S-O; q_O, the net negative charge associated with the oxygen atom, and θ, the bond angle of O-S-O. Table 2 shows the observed and evaluated values of the dipole moments of these molecules. The results are satisfactory within the range of experimental error, although some discrepancy is found in the case of dimethyl sulfoxide.

In conclusion, we can safely say that the shift of the $SK\alpha$ transition energy is a direct measure of the number of the outer-shell electrons associated with a sulfur atom in the bonding state.

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[8] L. Pauling, "The Nautre of the Chemical Bond," 3rd ed., Cornell Univ. Press, New York (1960), p. 93.

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[10] Londolt-Börnstein, "Tabellen," Springer-Verlag, Berlin (1952), 6 Aufl. I/3, s. 446 and s. 716.

[11] *Ibid.*, 6 Aufl. I/2, s. 17.