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An X-Ray Emission Spectroscopic Investigation of the Chemical Bond of Sulfur. III. The Profile of S$K\beta$ Band in Sulfur Compounds

Yoshihito TAKAHASHI and Katsumasa YABE

Government Industrial Development Laboratory, Hokkaido, Higashi-tsukisamu, Sapporo

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The profile of the S$K\beta$ band in various sulfur compounds, including many organic compounds, was separated into peaks, and the wavelength values and the intensities of the separated peaks were discussed in relation to the chemical bonding. The band of sulfone and sulfoxide consists of three or four peaks. We named the peaks A, B, C (the strongest), and D, beginning from the longer-wavelength side. The relative intensity of the peak A (generally named $K\beta'$) increases as the number of valence electrons of the sulfur atom decreases. The peak B may be attributed to the non-polar single bond of sulfur in sulfone and sulfoxide. The clear peak, D, appears only in the band of sulfite and sulfoxide. The band of the compounds of thiourea type consists of two peaks. Using the results of the above study, the chemical structures of aldehyde-bisulfite adducts and 2-mercaptobenzimidazole, *etc.*, were discussed.

In a previous paper,[1] we reported a study of the number of valence electrons of the sulfur atom in compounds in relation to the shifts of the S$K\alpha$ wavelength. However, the S$K\alpha$ line has no direct relation to the valence electrons which are con-

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[1] T. Sato, Y. Takahashi and K. Yabe, This Bulletin, **40**, 298 (1967).

nected with the chemical bond, for the S$K\alpha$ line arises from the inner-shell electron transition (2p→1s). On the contrary, the S$K\beta$ band arises from the transition of the valence electron (valence level→1s), so the structure of the S$K\beta$ spectrum is greatly influenced by the chemical state of the attributed compounds.

Faessler and Schmid has reported that the S$K\beta$ band spectra of sulfates have peculiar structures, unlike the bands of sulfides and rhombic sulfur.[2] Schnell studied the structures of the $K\beta$ band spectra, together with the relative intensity of $K\beta$ to $K\alpha$, in the elements of sulfur, phosphor, silicon, and aluminum in various compounds.[3] Also, Wilbur and Gofman studied the S$K\beta$ spectra of comparatively many materials, stressing the intensity.[4] Besides, the SL bands (valence level→2p) of various compounds were investigated by Fischer and Baun.[5] However, no sufficiently systematic investigation of the S$K\beta$ spectra of various organic compounds and liquid samples has yet been made. Moreover, no separation of the S$K\beta$ band spectrum into its component peaks has ever been attempted.

Our purpose was to make clearer the relationship between the character of the chemical bond and the S$K\beta$ band structure.

Experimental

The spectra were obtained on the improved Rigaku-Denki K-3 Fluorescent X-ray Spectrograph. Its details have been presented in the previous paper.[1] However, the glancing angle, α (the take-off angle of the X-ray), was changed to 35°. A flat sodium chloride crystal ($2d$: 5.6396 Å) was used as the analyzing crystal. Two Soller slits were inserted into the light path; the one situated between the sample and the crystal was 10 cm long, with 0.15 mm spacing, while the other, between the crystal and the detector, was 5 cm long and had 0.10 mm spacing. The helium path was maintained using a flow of 2 l/min. The Machlett OEG-50S chromium target X-ray tube was usually operated at 40 kV, 30 mA.

In the measurements of most of the liquid samples, a liquid sample holder with a Mylar-film window (10 μ thick) was employed, but in the cases of concentrated sulfuric acid, sulfuryl chloride, and thionyl chloride, the Mylar-film window was replaced by a polyethylene film window (30 μ thick).

The band profile was obtained as follows: the X-ray intensities were measured for a minute at each 3′(2θ) stage, and then these intensities, each measured maximum intensity having been made the same values, were plotted against the wavelength. The background was measured at 129°00′(2θ) (5.0902 Å), on the longer-wavelength side of the S$K\beta$ band, because, on the the shorter-wavelength side of the S$K\beta$ band, the absorption edge is near the band and, moreover, its position varies with the kind of compound.

The wavelength of the band was determined within an accuracy of ±0.0008 Å by referring to the third-order reflection lines of Ni$K\alpha_1$ (4.97352 Å) and Ni$K\alpha_2$ (4.98507 Å). On the measurement of the half-peakwidth, the half-linewidth of third-order reflection line of Ni$K\alpha_1$, 16.0′(2θ) (2.8 eV), was chosen as the standard.

Most of the sample materials were guaranteed or extra pure reagents. The materials which we prepared in our laboratory were confirmed by X-ray diffraction or infrared analysis. The surface temperatures of the samples were 30—40°C while the measurements were being carried out.

Results

The profiles of the S$K\beta$ band are related to the various bonding forms of the sulfur atom. We may divide them roughly into five classes according to the bonding form. The profiles of the S$K\beta$ band on several materials of each class are shown in Figs. 1—5, while the wavelength values, half-peakwidths, relative integrated intensities, and other data on the peaks of the S$K\beta$ band spectrum are listed in Tables 1—5.

1) Inorganic Sulfide. Except for cuprous sulfide, the S$K\beta$ spectra of ten inorganic sulfides

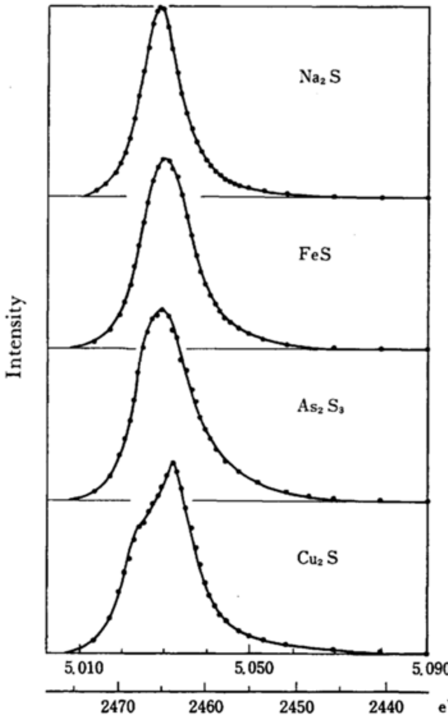

Fig. 1. S$K\beta$ spectra of inorganic sulfides.

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[2] A. Faessler and E. D. Schmid, *Z. Physik*, **138**, 71 (1954).

[3] E. Schnell, *Monatsh. Chem.*, **94**, 703 (1963).

[4] D. W. Wilbur and J. W. Gofman, "Advances in X-Ray Analysis," Vol. 9, ed. by Mallett, Fay, and Mueller, Plenum Press, New York (1965) p. 354.

[5] D. W. Fischer and W. L. Baun, *ibid.*, Vol. 9, p. 329.

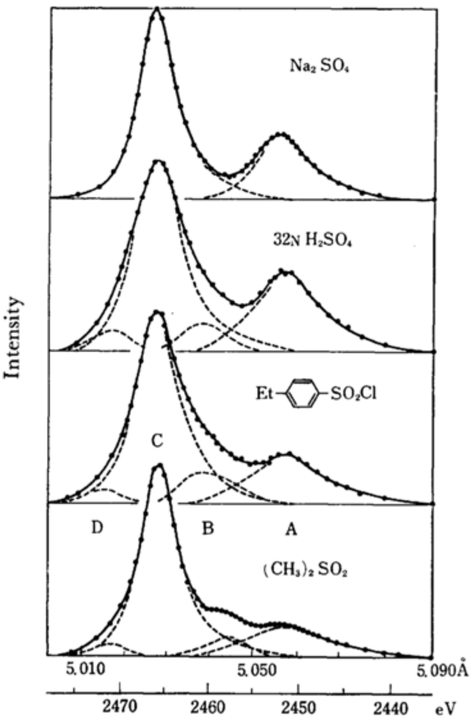


Fig. 2. S$K\beta$ spectra of sulfates and sulfones.

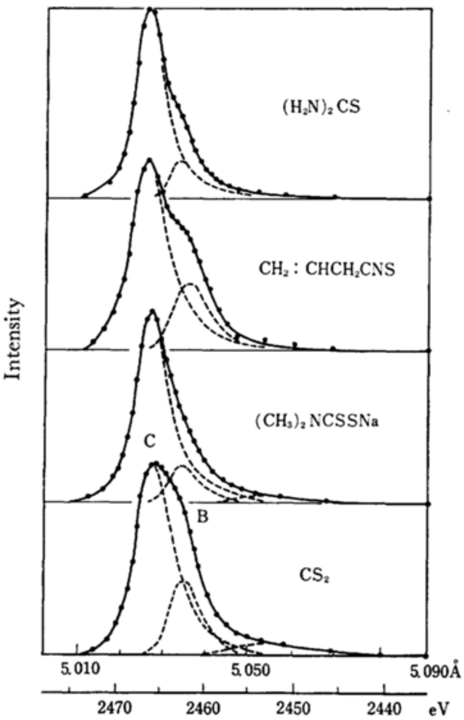


Fig. 4. S$K\beta$ spectra of thiourea, carbon disulfide, *etc.*

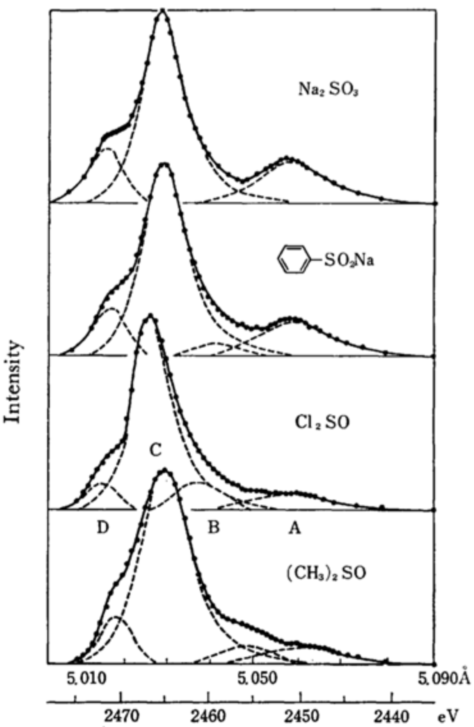


Fig. 3. S$K\beta$ spectra of sulfites and sulfoxides.

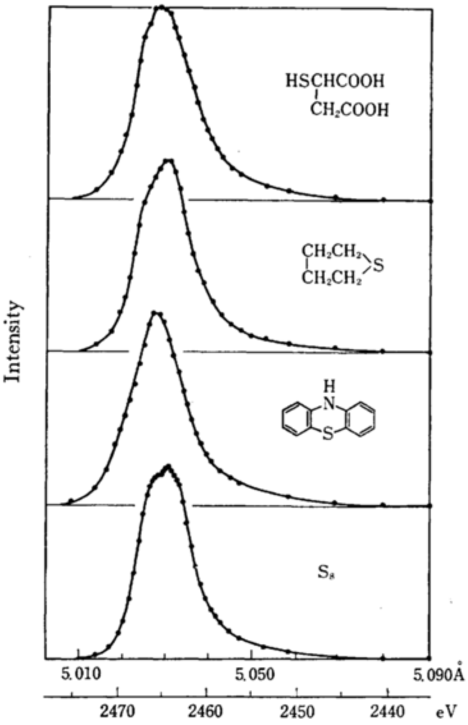


Fig. 5. S$K\beta$ spectra of thiol, organic sulfides and rhombic sulfur.

TABLE 1. WAVELENGTHS HALF-WIDTHS AND ASYMMETRY INDEXES OF PEAK IN $SK\beta$ SPECTRA OF INORGANIC SULFIDES

Compound	Coordination number*	Wavelength (Å)	Width (1/2)	Asymmetry index
Na_2S	8	5.0293	2.01	1.07
CaS	6	299	2.20	1.05
Cr_2S_3	6	297	2.33	1.06
α-MnS	6	295	2.60	1.07
ZnS	4	289	2.42	1.10
CdS	4	289	2.27	1.11
FeS**	6	304	2.54	1.05
NiS	6	304	2.58	1.05
Sb_2S_3		285	2.68	1.15
As_2S_3		285	2.79	1.20
Cu_2S**		32	2.9	
Error		±0.0008	±0.10	±0.03

* The number related to sulfur atom.

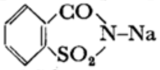
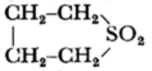
** Lack in sulfur content is an extent of about 1.0 wt %.

are almost identical in shape, but they slightly differ in position and in the width of the band. From their simple profiles, it can be assumed that the $SK\beta$ spectrum of inorganic sulfide consists of only one peak. The peaks of sulfides in which the coordination number of sulfur atom is six show a little longer-wavelength values and smaller asymmetry indexes than those of the other sulfides.

2) Sulfate and Sulfone. In Figs. 2—4, the dotted lines show the results obtained by the separation into peaks, using the profile of the $SK\beta$ band of sodium sulfide (shown in Fig. 1) as the standard shape of a single peak. A peak profile of an arbitrary size was made by lengthening or shortening the standard single peak in the direction of the ordinate or abscissa, while keeping the degree of asymmetry unchanged. Each of their spectra consists of two, three, or four peaks, which are named as A, B, C, and D beginning from the longer-wavelength side.

3) Sulfite and Sulfoxide. A feature of this class is the appearance of a remarkable peak D. The relative intensities of the peak A in this class generally take smaller values than those in the

TABLE 2. WAVELENGTHS HALF-WIDTHS AND RELATIVE INTENSITIES OF PEAKS IN $SK\beta$ SPECTRA OF SULFATES AND SULFONES

Compound	Wavelength (Å)				Width (½)		Intensity			
	A	B	C	D	A	C	A	B	C	D
Na_2SO_4	5.055		5.0262		2.6	1.9	0.30		0.70	
2M Na_2SO_4	5.055	5.038	5.0266	5.012	2.8	2.3	0.29	0.01	0.69	0.01
8N H_2SO_4	55	35	260	13	2.8	1.9	0.30	0.03	0.66	0.01
32N H_2SO_4	56	34	262	15	3.0	2.5	0.30	0.06	0.62	0.02
$NaHSO_4$	55	35	260		2.7	2.0	0.29	0.03	0.68	
$CaSO_4$	55		265		2.8	1.8	0.32		0.68	
$(NH_4)_2SO_4$	55	35	258		2.8	1.9	0.28	0.02	0.70	
$PhNH_2 \cdot ½H_2SO_4$	55	34	258		2.9	2.0	0.31	0.03	0.66	
$(EtO)_2SO_2$	56	37	264	16	3.3	2.5	0.30	0.05	0.61	0.04
$C_{12}H_{25}OSO_3Na$	56	35	259	14	3.2	2.2	0.31	0.02	0.66	0.01
$PhOSO_3K$	55	34	255		3.1	1.9	0.31	0.05	0.64	
H_2NSO_3H	55	34	262		2.8	1.9	0.29	0.03	0.68	
$HOCH_2SO_3Na$	57	41	270	12	3.2	2.0	0.27	0.03	0.67	0.03
$PhSO_3H$	56	38	268	16	3.3	2.3	0.26	0.05	0.66	0.03
$PhSO_2NH_2$	55	36	270	14	3.9	2.2	0.24	0.04	0.70	0.02
$PhSO_2NHBu$	55	38	270	14	3.3	2.3	0.24	0.09	0.65	0.03
p-$EtPhSO_2NEt_2$*	57	38	268	16	3.0	2.3	0.21	0.12	0.66	0.01
	55	38	277	16	4.0	2.4	0.24	0.06	0.65	0.05
Cl_2SO_2	55	35	257	12	3.7	2.0	0.27	0.07	0.65	0.01
p-$EtPhSO_2Cl$	56	38	264	14	3.8	2.2	0.24	0.10	0.63	0.03
$PhSO_2F$	56	37	266	16	3.8	2.6	0.24	0.08	0.64	0.04
$(CH_3)_2SO_2$	56	43	268	16	4.0	2.0	0.20	0.05	0.72	0.03
	57	41	274	16	3.8	2.3	0.19	0.08	0.68	0.05
Ph_2SO_2	57	40	274	16	3.7	2.2	0.21	0.08	0.68	0.03
Error	±0.001	±0.001	±0.0008	±0.002	±0.2	±0.1	±0.02	±0.03	±0.02	±0.03

* Benzene solution, 50%.

TABLE 3. WAVELENGTHS, HALF-WIDTH AND RELATIVE INTENSITIES OF PEAKS IN S$K\beta$ SPECTRA OF SULFITES AND SULFOXIDES

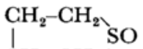
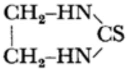
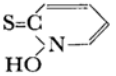
Compound	Wavelength (Å)				Width (1/2)		Intensity			
	A	B	C	D	A	C	A	B	C	D
Na_2SO_3	5.058		5.0288	5.016	3.3	2.2	0.20		0.66	0.14
$NaHSO_3$	5.059	5.039	5.0288	5.016	3.7	2.2	0.21	0.03	0.67	0.09
$(EtO)_2SO$	59	40	277	16	3.7	2.6	0.18	0.06	0.68	0.06
$HOCH_2SO_2Na$	58	41	283	16	3.4	2.3	0.16	0.02	0.75	0.07
$PhSO_2Na$	57	40	280	15	3.5	2.3	0.18	0.03	0.69	0.10
PhNSO	58	38	288	18	4.0	2.3	0.17	0.04	0.70	0.09
Cl_2SO	58	36	260	14	3.8	2.0	0.15	0.08	0.72	0.05
$(CH_3)_2SO$	60	47	280	17	4.0	2.6	0.09	0.05	0.75	0.11
	57	42	278	17	3.8	2.2	0.14	0.05	0.74	0.07
Error	±0.001	±0.001	±0.0008	±0.002	±0.2	±0.1	±0.02	±0.03	±0.02	±0.03

TABLE 4. WAVELENGTHS, HALF-WIDTHS AND RELATIVE INTENSITIES OF PEAKS IN S$K\beta$ SPECTRA OF ISOTHIOCYANATES, THIOUREA, *etc.*

Compound	Wavelength (Å)		Width (1/2)		Intensity	
	B	C	B	C	B	C
$CH_2{:}CHCH_2NCS$	5.036	5.0255	1.8	1.9	0.23	0.77
PhNCS	36	260	1.6	1.9	0.16	0.84
$(H_2N)_2CS$	33	255	1.3	1.5	0.14	0.86
	34	262	1.5	1.5	0.15	0.85
$(PhHN)_2CS$	34	265	1.7	1.5	0.23	0.77
$[(H_3C)_2N]_2CS$	34	267	1.5	1.5	0.18	0.82
$[(H_3C)_2NPh]_2CS$	34	272	1.9	1.9	0.21	0.79
$(H_3C)(H_2N)CS$	34	270	1.7	1.5	0.17	0.83
 $H_2NCS-CSNH_2$	33	265	2.0	1.8	0.25	0.75
	32	255	2.0	1.8	0.25	0.75
CS_2	33	262	1.6	2.0	0.23	0.77
KSCN	34	253	2.0	1.5	0.26	0.74
$Et_2NCSSNa$	33	260	1.9	1.6	0.17	0.83
$(O_2NPhO)(EtO)_2PS$*	36	288	2.0	2.0	0.17	0.83
Error	±0.001	±0.0008	±0.2	±0.1	±0.02	±0.02

* Kerosene solution, 50%.

sulfate and sulfone class.

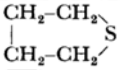
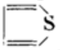
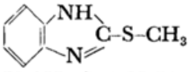
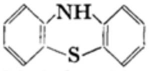
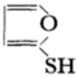
4) Thiourea Derivatives, Thiocyanates, Isothiocyanates, and Monothiophosphate (Abbr.: Thiourea Class). Each of their spectra consists of two main peaks, but in certain cases, as when a large tail exists on the longer-wavelength side, there seems to be another very weak peak.

5) Organic Sulfide, Thiol and Rhombic Sulfur. All of their spectra have broader bands. As with thiophene and phenothiazine, the spectrum of the compounds with a sulfur atom in unsaturated ring shows a prominent inflection on the shorter-wavelength side of the band.

Discussion

Inorganic Sulfide. The relationship between the S$K\beta$ bandwidth and the ionic character of the

TABLE 5. WAVELENGTHS OF PEAKS IN S$K\beta$ SPECTRA OF ORGANIC SULFIDES, THIOLS AND RHOMBIC SULFUR

Compound	Wavelength (Å)
	5.0285
	285
$[CH_2(OH)CH_2]_2S$	274
Ph_2S	282
	275
$PhCH_2$–S–C(NH_2)NH	265
	270
Methylene blue	280
HS–CH_2COONa	275
HS–Ph	285
o-HS–PhCOOH	280
HS–$(CH_2)_{15}CH_3$	301
HS–CH(COOH)CH_2COOH	270
	280
$(PhCH_2S–)_2$	265
$(ClS–)_2$	285
$(–CH_2S–)_3$	270
S_8	295
Error	0.0008

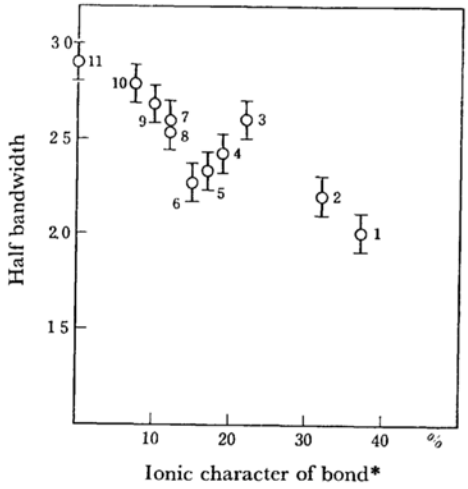


Fig. 6. Relationship between bandwidth of S$K\beta$ and ionic character of bond.

1 Na_2S, 2 CaS, 3 α-MnS, 4 ZnS, 5 Cr_2S_3, 6 CdS, 7 NiS, 8 FeS, 9 Sb_2S_3, 10 As_2S_3, 11 HS–CH_2COONa

* Ionic characters were calculated by the following equation,[6)]
Ionic character (%) $= 16|X_a-X_b| + 3.5|X_a-X_b|^2$, X_a, X_b: electronegativity of element.

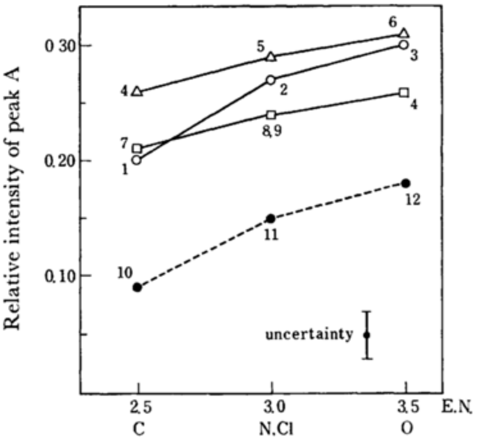


Fig. 7. Relationship between relative intensity of peak A and kind of atom combined with sulfonyl and sulfinyl group.

1 $(CH_3)_2SO_2$, 2 Cl_2SO_2, 3 $(EtO)_2SO_2$, 4 $PhSO_3H$, 5 H_2NSO_3H, 6 $C_{12}H_{25}OSO_3Na$, 7 Ph_2SO_2, 8 p-$EtPhSO_2Cl$, 9 $PhSO_2NH_2$, 10 $(CH_3)_2SO$, 11 Cl_2SO, 12 $(EtO)_2SO$

—— sulfone ------ sulfoxide

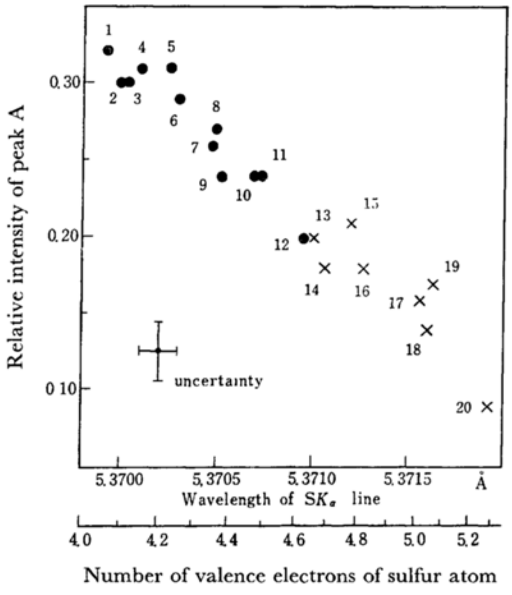


Fig. 8. Relationshop between relative intensity of peak A and number of valence electrons of sulfur atom.

1 $CaSO_4$, 2 $(EtO)_2SO_2$, 3 Na_2SO_4, 4 $PhNH_2\cdot\frac{1}{2}H_2SO_4$, 5 $C_{12}H_{25}OSO_3Na$, 6 H_2NSO_3H, 7 $PhSO_3H$, 8 $HOCH_2SO_3Na$, 9 $PhSO_2F$, 10 $PhSO_2NH_2$, 11 p-$EtPhSO_2Cl$, 12 $(CH_3)_2SO_2$, 13 Na_2SO_3, 14 $PhSO_2Na$, 15 $NaHSO_3$, 16 $(EtO)_2SO$, 17 $HOCH_2SO_2Na$, 18 $(CH_2)_4SO$, 19 PhNSO, 20 $(CH_3)_2SO$

● sulfone, × sulfoxide.

Wavelength values of S$K\alpha$ line were refered from Ref. 7.

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6) N. B. Hannay and C. P. Smyth, *J. Am. Chem. Soc.*, **68**, 171 (1946).

bond is shown in Fig. 6. As the ionic character of the bond increases, the bandwidth becomes narrower. On rhombic sulfur and organic sulfide, taken for reference, their S*Kβ* bandwidths show the values to be expected from Fig. 6.

The S*Kβ* band of cuprous sulfide takes a unique shape (see Fig. 1). It may be that its prominent shoulder on the shorter-wavelength side of the main peak is caused by the conduction electrons. Cuprous sulfide exhibits a highly electronic conductivity.

Sulfate, Sulfone, Sulfite and Sulfoxide. Concerning the energy differences between the peaks A and C in the S*Kβ* band spectrum, no noticeable distinction can be found among the sulfates, sulfones, sulfites, and sulfoxides measured at about 14 eV. Since no peak corresponding to A can be found in the S*Kβ* spectrum of sulfur compounds except for oxocompounds of sulfur, and since the energy difference varies almost not at all with the compound, the peak A may be attributed to the SO bond.

Figure 7 shows that the relative intensity of the peak A increases as the electronegativity value of the atom that is combined with the sulfonyl or sulfinyl group increases. In other words, as the plus charge on the sulfur atom increases, the intensity of the peak A increases. Figure 8 shows the relationship between the relative intensity of the peak A and the effective charges of the sulfur atom in sulfone and sulfoxide.[1] In Fig. 7, with regard to the relative intensity of the peak A of the sulfones and sulfoxides which have the same functional group (for example, $(EtO)_2SO_2$ and $(EtO)_2SO$, Cl_2SO_2 and Cl_2SO, $(CH_3)_2SO_2$ and $(CH_3)_2SO$, *etc.*), the former have values about twice as large as the latter. This fact shows that the increase in the relative intensity of the peak A is mainly influenced by the oxygen atom in the double bond. Therefore, with regard to the relative intensity of the peak A, comparing alkyl sulfate with alkyl sulfone and alkyl sulfite with alkyl sulfoxide, diethyl sulfate has twice as many oxygen atoms in a molecule as dimethyl sulfone, but the relative intensity of diethyl sulfate is considerably smaller than twice the value of dimethyl sulfone; moreover, though diethyl sulfite has three times as many oxygen atoms in a molecule as dimethyl sulfoxide, the relative intensity of the former is considerably smaller than three times the value of the latter. These facts show that, in the contribution to the increase in the relative intensity of the peak A, the oxygen atom in the single bond is smaller than that in the double bond. Assuming that the alkyl group scarcely contributes at all to the electron transfer, the above facts can be explained in terms of the concept that the inductive effect of the oxygen atom in the double bond is much larger than that of the oxygen atom in the single bond.

Most sulfones and sulfoxides have the peak B between the peaks A and C in the S*Kβ* spectra. The sulfone combined with the same two functional groups has a symmetrical peak B in the spectrum. On the other hand, the sulfone combined with two different groups has a partly asymmetrical peak B, which might consist of two peaks. Figure 9 shows

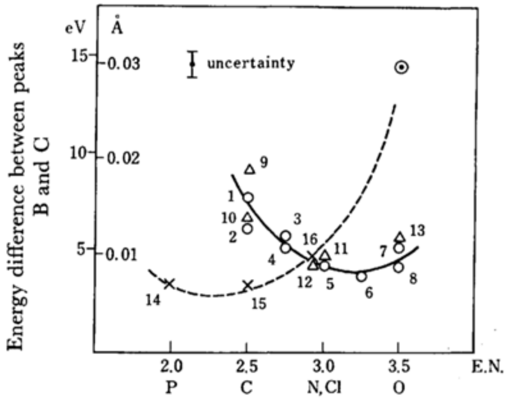


Fig. 9. Behavior of peak B.

1 $(CH_3)_2SO_2$, 2 Ph_2SO_2, 3 *p*-$EtPhSO_2Cl$,
4 $PhSO_2NH_2$, 5 Cl_2SO_2, 6 H_2NSO_3H,
7 $(EtO)_2SO_2$, 8 $C_{12}H_{25}OSO_3Na$, 9 $(CH_3)_2SO$,
10 $(CH_2)_4SO$, 11 Cl_2SO, 12 PhNSO,
13 $(EtO)_2SO$
○ sulfone, △ sulfoxide.

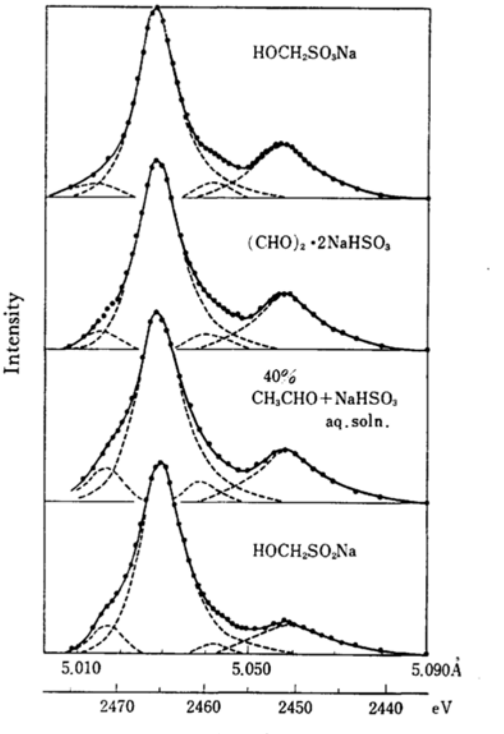


Fig. 10. Comparison of S*Kβ* spectra of aldehyde-bisulfite adducts with sulfone and sulfoxide.

Table 6. Comparison of S$K\beta$ spectra of aldehyde-bisulfite adducts with sulfones and sulfoxides

Compound	S$K\alpha$ Wavelength (Å)*	S$K\beta$			
		Wavelength (Å)		Intensity	
		A	C	A	D
$NaHSO_4$	5.36999	5.055	5.0260	0.29	
$HOCH_2SO_3Na$	7049	57	270	0.27	0.03
$HCHO+NaHSO_3$**	708	57	272	0.25	0.05
$CH_3CHO+NaHSO_3$**	709	57	275	0.24	0.07
$(CHO)_2\cdot 2NaHSO_3$	7053	57	272	0.26	0.03
$PhCHO\cdot NaHSO_3$	7049	57	280	0.27	0.05
$HOCH_2SO_2Na$	7157	58	283	0.16	0.07
$NaHSO_3$	7120	59	288	0.21	0.09
Error	±0.0001	±0.001	±0.0008	±0.02	±0.03

* Ref. 7.

** Aquous solution, 50%, estimated in adduct, keeping aldehyde excess.

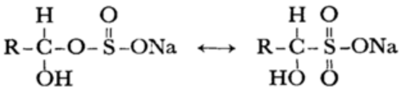
the relationship of the energy difference between the peaks B and C to the kind of atom combined with the sulfonyl and sulfinyl groups. There is no clear distinction in the energy difference among the elements of chlorine, nitrogen, and oxygen, but on carbon the peak B appears further apart from the peak C than in the cases of the other elements. In the compounds combined with amino or hydroxyl groups, the reltive intensity of the peak B is generally small (see Tables 2 and 3). The hydrogen atom in an amino or hydroxyl group is rather dissociable. A more dissociable group, such as –ONa, contributes very little to the intensity of the peak B. In sulfonamides, the relative intensity of the peak B is larger in the order: tertiary, secondary, and primary amino groups. This order is the reverse of the order of the number of dissociable hydrogen atoms in the amino group. These facts suggest that the evolution of the peak B is more affected by the non-polar single bond of sulfur in sulfone and sulfoxide.

In the spectrum of sodium bisulfite (see Fig. 3), a weak peak B is observed, so its hydroxyl group seems not to be very dissociable.

In the spectrum of concentrated sulfuric acid, the peak B is also observed; the peakwidth and the relative intensity of the peak are similar to those of diethyl sulfate rather than to those of diluted sulfuric acid or sodium sulfate (see Table 2). Consequently, the hydroxyl groups of concentrated sulfuric acid seem to be rather undissociable.

The appearance of the peak D is clear only in the spectra of sulfites and sulfoxides. But then, the peak corresponding to the peak D of sulfur compounds has been observed in the B$K\alpha$ band spectra of boric oxide $(B_2O_3)_n$ and boric nitride $(BN)_n$.[5] The boron atom in their compounds has a sp^2 hybrid orbital, analogous with the sulfur atom in a sulfite ion. Therefore, the peak D may result from the presence of the sp^2 hybrid orbital. In the spectra of some sulfones, a very weak peak like D was separated by the separation into peaks.

The S$K\beta$ spectra of aldehyde-bisulfite adducts are shown in Fig. 10. Their peak C shifts about 0.001 Å to the shorter-wavelength side from the position of bisulfite salt or sodium formaldehyde sulfoxylate ($HOCH_2SO_2Na$), and the relative intensities of the peak A are larger, and those of the peak D are smaller, than those of sulfites and sulfoxides (see Table 6). These take values rather closer to those of such sulfones as hydroxymethansulfonate ($HOCH_2SO_3Na$). Moreover, the wavelength of the S$K\alpha$ line of the adducts take values closer to those of sulfones. Two structural formulas in the equilibrium state may be given for the aldehyde-bisulfite adduct;



$$R-\overset{H}{\underset{OH}{C}}-O-\overset{O}{\overset{\|}{S}}-ONa \longleftrightarrow R-\overset{H}{\underset{HO}{C}}-\overset{O}{\underset{O}{S}}-ONa$$

(I) (II)

According to this fact, a considerable portion of the materials have sulfone-type structures (II). This conclusion is supported by the results of the X-ray structural analysis.[8]

Thiourea Class. The values of the energy differences between the peaks B and C range from 3 to 5 eV, much as with those of sulfones. However, it cannot be asserted that this peak B has virtually the same quality as those of sulfones because the two bonding forms which seem to be attributable to the peak B are different; that is, in sulfnones,

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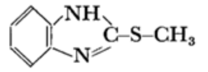
7) Y. Takahashi, K. Yabe and T. Sato, This Bulletin, **42**, 2707 (1969).

8) T. Kuroda, T. Ashida, Y. Sasada and M. Kakudo, *ibid.*, **40**, 1377 (1967).

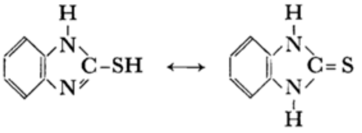
TABLE 7. COMPARISON OF S$K\beta$ SPECTRA OF 2-MERCAPTOBENZIMIDAZOLE AND ITS HOMOLOGS WITH THIOUREA AND THIOLS

Compound	S$K\alpha$ Wavelength (Å)	S$K\beta$				
		Wavelength (Å)		Width (1/2)		Intensity B
		B	C	B	C	
2-Mercaptobenzimidazole	5.37302*	5.034	5.0262	1.6	1.4	0.19
2-Mercaptobenzimidazole pyridine soln., 40%	*	34	258	1.5	1.3	0.17
2-Mercaptobenzoxazole	7308*	34	258	1.7	1.4	0.19
2-Thiobarbituric aicd	7298*	34	258	1.7	1.5	0.21
2-Thiouracil	7301*	34	258	1.3	1.5	0.19
$(H_2N)_2CS$	7287*	33	255	1.3	1.5	0.14
$(PhHN)_2CS$	731**	34	265	1.7	1.5	0.23
o-HS–PhCOOH	728**		280		2.7	
HS–CH_2COONa	728**		275		2.9	
	7283*		275		2.7	
Error	±0.0001	±0.001	±0.0008	±0.2	±0.1	±0.02

* Ref. 7. ** Ref. 1.

there is a single bond, and in the thiourea class, a double bond.

On 2-mercaptobenzimidazole, 2-mercaptobenzoxazole, 2-thiouracil, and 2-thiobarbituric acid, we can assume two structural formulas, *i. e.*, thiol and thiocarbonyl forms. For example, 2-mercaptobenzimidazole may have the following two forms:



(III) (IV)

However, in the solid state and in a pyridine solution, its S$K\beta$ spectrum differs from those of thiols and is similar to those of thiocarbonyl-type compounds, as is shown in Fig. 11. Furthermore, the wavelengths of the S$K\alpha$ lines also have values closer to that of thiourea. Consequently, they may be said to have thiocarbonyl forms (IV) in the solid state and in a pyridine solution at room temperature.

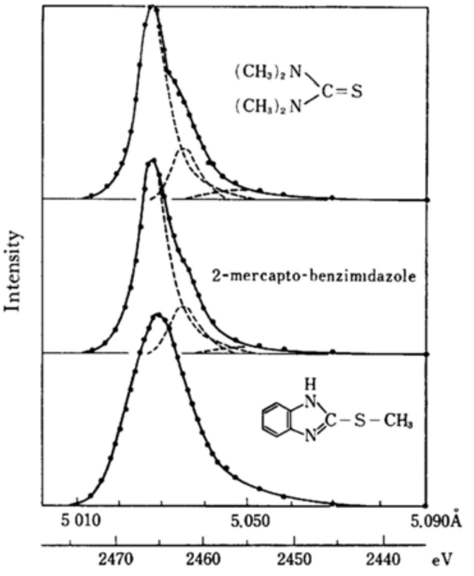


Fig. 11. Comparison of S$K\beta$ spectra of 2-mercaptobenzimidazole with thiourea and 2-methylthiobenzimidazole.

Conclusion

In this study, we found that S$K\beta$ spectra give appreciable information relating not only to the kind of bonding but also to the kind of atom combined with the sulfur atom in compounds. Especially, we have obtained much information on sulfones and sulfoxides. If the separation into peaks were more accurate, a more detailed discussion could be made with respect to the peaks B and D, thus making the analysis of the bonding state feasible, even in a mixture.

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