BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2039—2044 (1973)

The X-Ray Emission Spectra of the Compounds of Third-period Elements. VI.* The Relationship between the $K\alpha$ and $K\beta$ Spectra

Yoshihito TAKAHASHI

Government Industrial Development Laboratory, Hokkaido, 41-2 Higashi-Tsukisamu, Toyohira, Sapporo 061-01

(Received December 4, 1972)

Data on the $K\beta$ spectra for several compounds of silicon, aluminum, and sulfur are shown. The intensity of the $K\beta'$ line is affected not by the kinds of thrid-period atoms, but by their charges and by the kinds of ligand atoms. The degree of the contribution of each bonding group to the relative intensity of the $K\beta'$ line and to the chemical shift of the $K\alpha_{1,2}$ lines are shown; they have additivity in the molecule. Therefore, the chemical shift of the $K\alpha_{1,2}$ lines can be estimated from the molecular structural formula; the charge of the atom can also be estimated.

Concerning some compounds of sulfur,[3] chlorine,[4] and phosphorus,[5] the fine structures of the $K\beta$ spectra have been investigated with relation to the chemical bonds. On these oxygen-included compounds, a satellite line, $K\beta'$ line, is observed in the spectrum; the relative intensity of the satellite line is related to the energy shift of the $K\alpha_{1,2}$ lines. In addition, it has been

* Our papers first named "An X-Ray Emission Spectroscopic Investigation of the Chemical Bond of Sulfur I~III"[1-3] have been renamed Parts III~V of this series.

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

2) Y. Takahashi, K. Yabe, and T. Sato, *ibid.*, **42**, 2707 (1969).

3) Y. Takahashi and K. Yabe, *ibid.*, **42**, 3064 (1969).

4) Y. Takahashi, *ibid.*, **44**, 587 (1971).

5) Y. Takahashi, *ibid.*, **45**, 4 (1972).

reported that the $K\beta'$ line is also observed in the spectra of compounds of third-period elements in which electronegative elements other than oxygen, such as fluorine, chlorine, and nitrogen, are included as ligands.[6-8] In order to check the character of the $K\beta'$ line and other satellite lines in detail, in this paper the characteristics of the K spectra of several compounds of silicon and aluminum, and also these of a few fluoro-compounds of sulfur and phosphorus, will be discussed.

Many reports have been published on the spectra of the compounds of silicon and aluminum;[6,7,9-11] these reliable reports shall be referred to in this paper as much as necessary. However, in order to compare the band-width and the chemical shift of the line, some easily measurable data were measured anew, consistently with some of the new data, such as those on tetraethylorthosilicate, silicon tetrachloride, aluminium propoxide, sulfur tetrafluoride, by means of our own apparatus.

Experimental

The details of the measurement apparatus and the conditions were presented in previous papers.[1,3] Analyzing crystals were used: EDDT (020) for the measurements of the Si and Al K spectra, germanium (111) for the P K spectra, and sodium chloride (200) for the S K spectra. In the measurements of gaseous samples, the samples were made to flow through a cell at a steady pressure. The gas-sample cell is a stainless-steel vessel with Mylar film window 25 mm × 30 mm, and 25 mm in depth.

The separation of the $K\beta$ spectrum into component peaks was done in a manner similar to that described in previous paper,[3-5] adopting the P $K\beta_1$ line of anhydrous sodium phosphate[5] as the standard shape of the component peak. Previously, we adopted the S $K\beta_1$ line of anhydrous sodium sulfide as the standard shape in peak separation for the S $K\beta$ spectra.[3] However, concerning the peak separation for two sulfur fluoro-compounds, we could find little difference between the results of the two methods.

Results and Discussion

Silicon Compounds. The Si $K\beta$ spectra of the compounds which were measured are shown in Fig. 1. The characteristic values on the $K\alpha_{1,2}$ and the $K\beta$ lines for each compound are listed in Table 1. The chemical shifts of the $K\alpha_{1,2}$ lines were determined with silicon metal as the standard material.

The energy differences between the $K\beta_1$ line (C peak) and the $K\beta'$ line (A peak) are about 14 eV for oxy-compounds, 19 eV for sodium hexafluorosilicate, and 8.6 eV for silicon tetrachloride.

The Si $K\beta$ spectrum of silicon dioxide consists of two main peaks; the $K\beta_1$ (C) and the $K\beta'$ (A). The

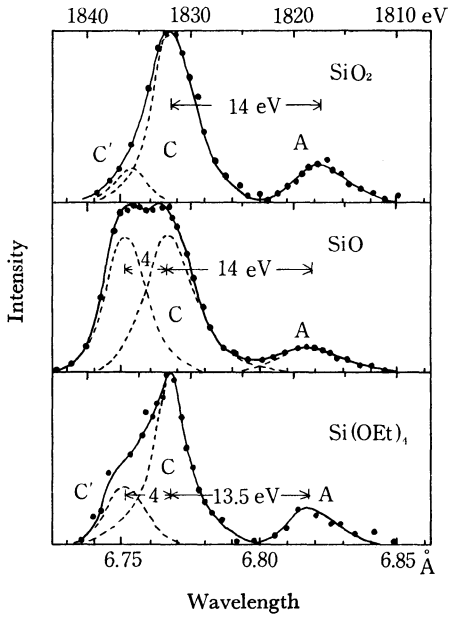

Fig. 1a. Silicon $K\beta$ spectra of some silicon compounds
A: $K\beta'$ line, C: $K\beta_1$ line.

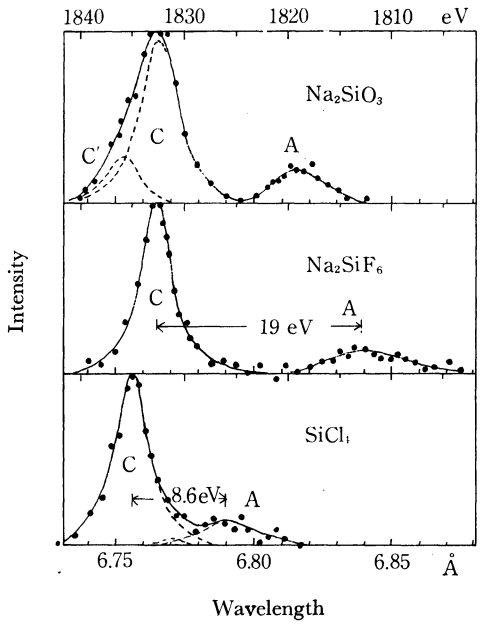

Fig. 1b. Silicon $K\beta$ spectra of some silicon compounds
A: $K\beta'$ line, C: $K\beta_1$ line.

$K\beta_1$ line is about 1.4 times wider than those of the spectra of sodium hexafluorosilicate and silicon tetrachloride. It seems that the spectrum contains a satellite line which is like the C' peak in the P $K\beta$ spectra of molecular phosphorus compounds.[5]

The C peak in the spectrum of silicon monoxide[13] seems to consist of two component peaks. White said that the component peak on the short-wavelength side was the $K\beta_1$ line, which was attributable to the zero valent silicon atom, and that the other was the $K\beta_1$ line of the plus-4 valent silicon atom.[14]

6) K. Ohno, *Bunseki Kagaku*, **20**, 308 (1971).
7) D. F. Lawrence and D. S. Urch, *Specrtochim. Acta*, **25B**, 305 (1970).
8) W. L. Baun and D. W. Fischer, *ibid.*, **21**, 1471 (1965).
9) C. G. Dodd and G. L. Glen, *J. Appl. Phys.*, **39**, 5377 (1968).
10) E. W. White and G. V. Gibbs, *Amer. Mineralogist*, **52**, 985 (1967).
11) S. Maruno and S. Fujii, *Jap. J. Appl. Phys.*, **9**, 1428 (1970).
12) Landolt-Börnstein, "Zahlenwerte und Funktionen," 6 Aufl. I/4 (1952), S. 859.

Table 1. Chemical shift of the $K\alpha_{1,2}$ lines and characteristic values of the $K\beta$ spectrum of silicon compounds

Compound	$K\alpha_{1,2}$ Chemical shift (eV)	$K\beta$ Peak position (eV)			$K\beta$ Relative intensity	
		A	C	C′	A	C′
SiO_2	0.72	1818.4	1832.4	1835.6	0.18	0.11
SiO	0.40	18.1	31.8	36.2	0.12	0.40
$Si(OEt)_4$	0.68	17.9	31.8	35.6	0.16	0.19
Na_2SiO_3	0.66	18.4	32.6	35.6	0.16	0.16
$Al_2(SiO_3)_3$	0.75	18.4	23.1	35.4	0.18	0.17
Na_2SiF_6	1.05	13.6	32.6		0.19	
$SiCl_4$	0.66	26.8	35.4		0.18	
σ	0.06	0.3	0.3		0.02	0.03
SiC	0.22[a]				0.19[b]	

a) Ref. 12.
b) The value was estimated from the spectrum of Ref. 15.

Tetraethylorthosilicate ($Si(OEt)_4$) and sodium metasilicate (Na_2SiO_3) are molecules which have tetrahedral structures,[15] and their silicon atoms do not have any lone pairs. Consequently, it is inferred that, in these spectra, the satellite peak which is so-called D peak does not appear.[17] In their spectra, the energy difference between the shorter-wavelength peak and the $K\beta_1$ line (C) is about 4 eV. This value is close to the energy difference between the $K\beta_1$ line (C) and the C′ peak in the P $K\beta$ spectrum of phosphorus pentoxide, 5 eV. On the other hand, the difference between the $K\beta_1$ line and the D peak is about 7 eV in the spectra

Table 2. Chemical shift of the $K\alpha_{1,2}$ lines and cha racteristic values of the $K\beta$ spectrum of aluminum compounds

Compound	$K\alpha_{1,2}$ Chemical shift (eV)	$K\beta$ Peak position (eV)		$K\beta$ Relative intensity
		A	C	A
Al_2O_3	0.41	1536	1553	0.11
$Al(OPr)_3$	0.37	1537	1553	0.14
AlF_3	0.64	1530	1550	0.12
AlF_3 (dry)	0.57	1532	1551	0.11
σ	0.07	0.5	0.5	0.03
Na_3AlF_6	0.52[a]	1531[b]	1552[b]	0.12[c]
AlN	0.29[a]			0.09[d]
Al_4C_3	0.13[a]			0.16[d]

a) Ref. 12.
b) Ref. 7.
c) The value was estimated from the spectrum of Ref. 7.
d) The value was estimated from the spectrum of Ref. 6.

13) 99.9%; it was produced by Nakarai Chemicals, Ltd.
14) E. W. White, *Solid State Commun.*, **2**, 151 (1964).
15) The structure of $Si(OEt)_4$ was determined by analogy with that of $Si(OMe)_4$.[16]
16) R. Kiriyama and H. Kiriyama, "Kozo-Mukikagaku, II," (1966), p. 213.
17) The D peak appears in the $K\beta$ spectrum of a compound in which the central atom has a lone pair, such as sulfite, sulfur tetrafluoride, and phosphorus trichloride.[5]

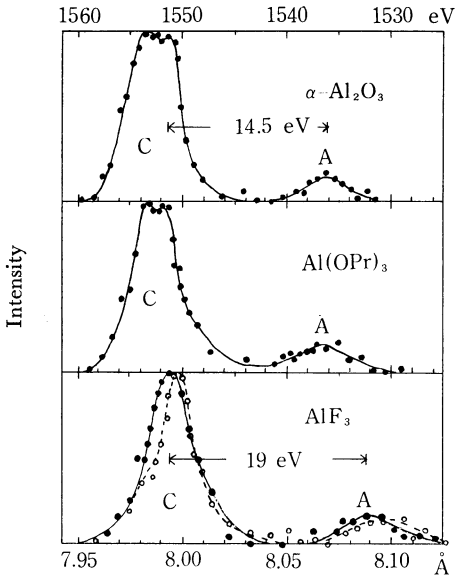

Fig. 2. Aluminum $K\beta$ spectra of some aluminum compounds
A: $K\beta'$ line, C: $K\beta_1$ line.

of sulfite, chlorite, and sulfur tetrafluoride. Hence, the shortest-wavelength peak may be the C′ peak.

Aluminum Compounds. The measured Al $K\beta$ spectra are shown in Fig. 2. The data on the $K\alpha_{1,2}$ lines and the $K\beta$ lines of each compound are listed in Table 2. The standard material for the $K\alpha_{1,2}$-line shifts is aluminium metal.

In the spectra of aluminum oxide and aluminum propoxide, the top of the $K\beta_1$ line splits into two peaks, so one may guess that the C′ peak exists in the spectrum. Concerning the spectrum of aluminum oxide, a theory has been advanced attributing the shorter-wavelength peak to the transition of the π-electron, and the longer one, to the σ-electron.[9] The differences between these peaks and the $K\beta'$ line (A) are 16 and 14.5 eV respectively.

The Al $K\beta$ spectrum of aluminum fluoride, the specimen of which was not dried enough (however, it was confirmed to be anhydride by X-ray diffraction), is different from that of the dried specimen and from that which was measured in the vacuum. In the former spectrum, a puff which seems to be the C′ peak is observed, but it is absent in the latter.

Sulfur and Phosphorus Compounds. The measured S $K\beta$ spectra of sulfur hexafluoride, sulfur tetrafluoride, and sulfur dioxide in a gaseous state are shown in Fig. 3. The energy differences between the $K\beta_1$ (C) and the $K\beta'$ (A) lines are 18.5, 17.8, and 15.5 eV for SF_6, SF_4, and SO_2 respectively. The D peak is observed in the spectra of SF_4 and SO_2. The characteristic values of the $K\alpha_{1,2}$ and the $K\beta$ lines for these sulfur compounds and potassium hexafluorophosphate (KPF_6), are listed in Table 3. As the standard materials for the line shift, rhombic sulfur and red phosphorus were chosen.

The $K\beta'$ Line in All the Measured Spectra. The values of the energy difference between the $K\beta_1$ and the $K\beta'$ lines in the oxy-compound are spread from

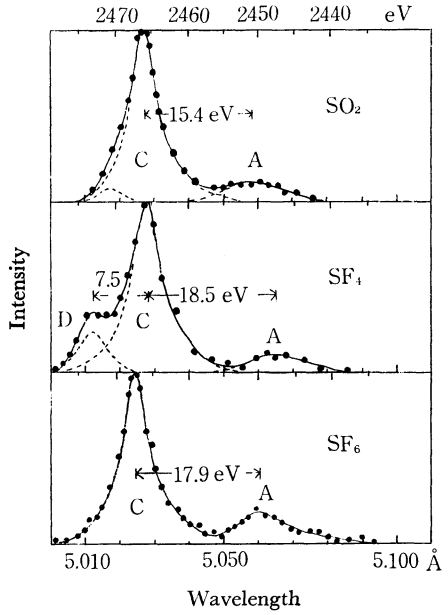

Fig. 3. Sulfur $K\beta$ spectra of some sulfur compounds
A: $K\beta'$ line, C: $K\beta_1$ line.

TABLE 3. CHEMICAL SHIFT OF THE $K\alpha_{1,2}$ LINES AND CHARACTERISTIC VALUES OF THE $K\beta$ SPECTRUM OF SOME SULFUR AND PHOSPHORUS COMPOUNDS

Compound	$K\alpha_{1,2}$ Chemical shift (eV)	$K\beta$ Peak position (eV)			$K\beta$ Relative intensity		
		A	C	D	A	C	D
SF_6	1.59	2449.2	2467.1		0.25	0.75	
SF_4	0.94	2447.3	2465.8	2473.6	0.15	0.72	0.13
SO_2	0.65	2451.1	2466.5	2470.7	0.16	0.79	0.05
KPF_6	0.87	2120[a]	2138[a]		0.2_0[b]	0.8_0[b]	
σ	0.04	0.5	0.4	1.0	0.02	0.02	0.03

a) Ref. 7.
b) The value was estimated from the spectrum of Ref. 7.

13.6 to 15.6 eV. Particularly, those of oxy-anions, such as ClO_4^-, ClO_3^-, SO_4^{2-}, and PO_4^{3-}, are less than 14 eV, while in many cases of molecular compounds, such as sulfone, sulfoxide, and SO_2, they are more than 14 eV.[3-5] On the other hand, in the cases of fluoro-compounds and chlorine-compounds (which have chlorine atoms as ligands), the values are 17.9~21 eV[7] and about 8.5 eV[5] respectively. According to Ohno's report,[6] in which several Al $K\beta$ spectra are given, the values are estimated to be about 12 eV for nitride and 8 eV for carbite. In the Si $K\beta$ spectrum, the value of carbite is 9 eV[18] (Table 4). Consequently, the energy difference between the $K\beta_1$ and the $K\beta'$ lines actually differs according to the kind of ligand atom.

The relationship between the relative intensity of the $K\beta'$ line (the ratio of the integral intensity of the A peak to that of the total of the $K\beta$ lines) and the chemical shift of the $K\alpha_{1,2}$ lines for each compound is shown in Fig. 4. In this figure, our results and those of some

18) G. Wiech, "Soft X-Ray Band Spectra," ed. by D. J. Fabian, Academic Press, London and New York (1968), p. 59.

TABLE 4. ENERGY DIFFERENCE BETWEEN $K\beta_1$ AND $K\beta'$ LINES

Compound	$\Delta E_{K\beta_1-K\beta'}$	Compound	$\Delta E_{K\beta_1-K\beta'}$
$NaClO_4$	13.6 eV	SF_6	17.9 eV
$NaClO_3$	13.6	SF_4	18.5
$NaClO_2$	14.3	KPF_6	18[a]
Na_2SO_4	14.0	Na_2SiF_6	19.0
$PhSO_3H$	14.2	AlF_3	19
$(EtO)_2SO_2$	14.4	Na_3AlF_6	21[a]
$(CH_3)_2SO_2$	14.2		
Na_2SO_3	14.2	PCl_5	8.5
$(CH_3)_2SO$	15.6	PCl_3	8.5
SO_2	15.4	$SiCl_4$	8.6
Na_3PO_4	13.9		
Na_2HPO_3	13.9	AlN	12[b]
NaH_2PO_2	14.2		
SiO_2	14.0	SiC	9[c]
Na_2SiO_3	14.2	Al_4C_3	8[d]

a) Ref. 7.
b) The value was estimated from the spectrum of Ref. 6.
c) The value was estimated from the spectrum of Ref. 15.

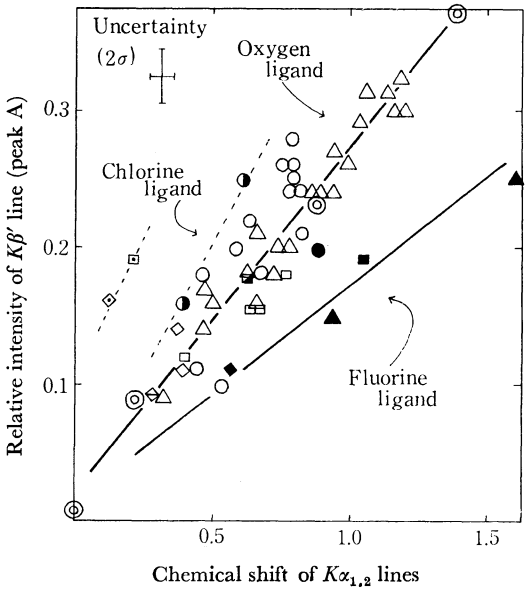

Fig. 4. Relationship between the relative intensity of $K\beta'$ line and the chemical shift of $K\alpha_{1,2}$ lines
◎: Chlorine compound, △, :▲ Sulfur compound, ○, ●, ◑: Phosphorus compound, □, ■, ◪: Silicon compound, ◇, ◆: Aluminum compound.
white point: Oxygen ligand compound, black point: Fluorine ligand compound, half-black point: Chlorine ligand compound.
⊡: SiC, ◈: Al_4C_3, ◈: AlN.

other researchers are collected. Two points are clear; the measured points make a linear relation for each ligand element, and these linear relations are almost independent of the kind of central atom in the molecule. It has become clearer, therefore, than in the results presented in a previous paper[4] that the intensity of the $K\beta'$ line is affected not by the kinds of central atoms, but by their charges, and by the kinds of ligand atoms. This deduction as to the effects of ligand elements is consistent with Nefedow's theory,[19] in which

19) W. I. Nefedow, *Zh. Strukt. Khim.*, **8**, 686, 1037 (1967).

Table 5. Contribution of an atom bonded with a sulfur atom to the relative intensity of S $K\beta'$ line and the chemical shift of S $K\alpha_{1,2}$ lines

=O	0.10 (0.38 eV)	-C	~0.00 (0.00 eV)
-O	0.05 (0.19)	-Cl	0.03 (0.12)
=N	0.07 (0.26)	-F	0.04 (0.26)
-N	0.04 (0.16)	lone pair	−0.02(−0.08)

( ): value for the contribution to the chemical shift of $K\alpha_{1,2}$ lines

he proposes that, in MO_4-type oxy-anions of third-period elements, the $K\beta'$ line is substantially due to the electronic transition from the O_{2s} state to the M_{1s} state.

Table 6. Contribution of an atom bonded with a chlorine atom to the relative intensity of Cl $K\beta'$ line and the chemical shift of Cl $K\alpha_{1,2}$ lines

=O	0.12	(0.46 eV)
-O	~0.00	(0.00)
lone pair	−0.02	(−0.08)

( ): value for the contribution to the chemical shift of Cl $K\alpha_{1,2}$ lines

Table 7. Contribution of an atom bonded with a phosphorus atom to the relative intensity of P $K\beta'$ line and the chemical shift of P $K\alpha_{1,2}$ lines

=O	0.14 (0.40 eV)	-Cl	0.05 (0.12 eV)
-O	0.04 (0.13)	-H	~0.00 (0.00)

( ): value for the contribution to the chemical shift of $K\alpha_{1,2}$ lines

Table 8. Comparison of the estimated value with the observed value on the relative intensity of S $K\beta'$ line

Compound	Rel. int. of $K\beta'$	
	Estd	Obsd[a]
Na_2SO_4	0.30	0.30
$(EtO)_2SO_2$	0.30	0.30
H_2NSO_3H	0.29	0.29
$PhSO_3H$	0.25	0.26
$(CH_3)_2SO_2$	0.20	0.20
SF_6	0.24	0.25
Cl_2SO_2	0.26	0.27
p-$EtPhSO_2Cl$	0.23	0.24
$PhSO_2NH_2$	0.24	0.24
$PhSO_2NHBu$	0.24	0.24
p-$EtPhSO_2NEt_2$	0.24	0.21
Na_2SO_3	0.18	0.20
$(EtO)_2SO$	0.18	0.18
$HOCH_2SO_2Na$	0.13[b]	0.16
$PhSO_2Na$	0.20[c]	0.18
$(CH_3)_2SO$	0.08	0.09
SF_4	0.14	0.15
Cl_2SO	0.14	0.15
SO_2	0.18	0.16
PhNSO	0.15	0.17

a) from Ref. 3.
b) The value was estimated as a thionyl compound.
c) The value was estimated as a sulfonyl compound.

Table 9. Comparison of the estimated value with the observed value on the chemical shift of $K\alpha_{1,2}$ lines

Compound	Chemical shift (eV)	
	Estd	Obsd
Na_2SO_4	1.14	1.15[a]
$(EtO)_2SO_2$	1.14	1.16[a]
H_2NSO_3H	1.11	1.04[a]
$PhSO_3H$	0.95	0.96[a]
$PhSO_2NH_2$	0.92	0.93[a]
$PhSO_2NHBu$	0.92	0.95[a]
p-Et-$PhSO_2NEt_2$	0.92	0.95[a]
Cl_2SO_2	1.00	0.99[a]
p-Et-$PhSO_2Cl$	0.88	0.85[a]
$(CH_3)_2SO_2$	0.76	0.75[a]
SF_6	1.56	1.59[a]
Na_2SO_3	0.68	0.74[a]
$NaHSO_3$	0.68	0.65[a]
$(EtO)_2SO$	0.68	0.61[a]
Cl_2SO	0.54	0.65[a]
$(CH_3)_2SO$	0.30	0.33[a]
PhNSO	0.56	0.46[a]
SO_2	0.68	0.65[a]
SF_4	0.96	0.94[a]
$HOCH_2SO_2Na$	0.49[c]	0.49[a]
$PhSO_2Na$	0.76[d]	0.70[a]
Na_3PO_4	0.79	0.79[b]
Na_2HPO_4	0.79	0.76[b]
NaH_2PO_4	0.79	0.80[b]
H_3PO_4	0.79	0.79[b]
$(P_2O_5)_2$	0.79	0.82[b]
$(PhO)_3PO$	0.79	0.70[b]
PCl_5	0.60	0.59[b]
$POCl_3$	0.76	0.58[b]
Na_2HPO_3	0.66	0.66[b]
H_3PO_3	0.66	0.59[b]
$(PhO)_3P$	0.39	0.54[b]
PCl_3	0.36	0.41[b]
NaH_2PO_2	0.53	0.48[b]
H_3PO_2	0.53	0.45[b]
$NaClO_4$	1.38	1.38[b]
$NaClO_3$	0.84	0.87[b]
$NaClO_2$	0.30	0.22[b]

a) from Ref. 2.
b) from Ref. 4 or 5.
c) The value was estimated as a thionyl compound.
d) The value was estimated as a sulfonyl compound.

The degree of the contribution of each bonding group which is linked to the sulfur atom to the relative intensity of the S $K\beta'$ line is shown in Table 5. The effects of these groups have additivity in each molecule. For example, in diethyl sulfate ($(EtO)_2SO_2$), the sulfur atom is linked by two double-bonded oxygen atoms and two single-bonded oxygen atoms, so the relative intensity of the $K\beta'$ line is estimated to be 0.30 ($2\times 0.10+2\times 0.05$); in benzenesulfonamide ($PhSO_2NH_2$), the sulfur atom is linked by two double-bonded oxygen atoms, one nitrogen atom (amino group), and one carbon atom (phenyl group), so the value is estimated to be 0.24 ($2\times 0.10+0.04+0.00$), and in sulfur dioxide, the sulfur atom has two double-bonds and one lone

pair, so the value is 0.18 ($2\times0.10-0.02$). These estimated values are in fair agreement with the observed values, 0.30, 0.24, and 0.16 respectively, in the stated order. This rule is almost consistent in all measured sulfur compounds (see Table 8). Similar relations are obtained in chlorine and phosphorus compounds (Tables 6 and 7). For example, assuming that phosphate, phosphite, and hypophosphite are tri-, di-, and mono-basic salts respectively, their estimated relative intensities in the P $K\beta'$ lines are 0.26, 0.22, and 0.18. These values coincide with the observed values. However, in regard to the phosphorus complex compounds, this rule is not entirely consistent.

Estimation of the Chemical Shift of $K\alpha_{1,2}$ Lines. Considering the relationship shown in Fig. 4, the contribution of the bonding group to the relative intensity of the $K\beta'$ line can be converted to the effect of the group on the chemical shift of $K\alpha_{1,2}$ lines. The converted value is shown in parentheses in Tables 5, 6, and 7. Some comparisons with the observed values of the estimated values of the chemical shift of the $K\alpha_{1,2}$ lines for molecules based on these converted values are shown in Table 9. Except for the atoms directly bonded to the sulfur atom, the next bonded atom may also be attributed to the chemical shift; however, its extent may not be very large, as is seen in the examples of benzenesulfonamide derivatives. The lone pair, as well as the bonding group, affects the screening of electrons for the atomic nuclear charges; hence, the chemical shift is influenced by the existence of the lone pair. If the contribution of the lone pair to the chemical shift is not taken, the coincidence of the estimated value with the observed value in the compound which has some lone pairs will become worse. In so far as the effective charges of an atom (not the total charges of an atom) are concerned, the effect of the lone pair should be separated from the charges of the atom. The results of Table 9 show that the chemical shift of the S $K\alpha_{1,2}$ lines, which relates to the charges of the sulfur atom,[1,20] can be estimated from the molecular structural formula, without any measurement of the wavelength of the $K\alpha_{1,2}$ lines. Therefore, we can temporarily estimate the charges of the atom in a molecule from the molecular structural formula.

Concerning sulfinate, two chemical structures are given; R–SO_2–Na and R–SO–ONa.[21] The comparison in Table 9 shows that benzenesulfinate may have the former structure (sulfonyl), while hydroxymethansulfinate may have the latter structure (thionyl).

The author wishes to thank Dr. Katsumi Ohno (National Institute for Metals), Dr. Toshio Sato, Mr. Katsumasa Yabe, and Mr. Tomiki Takahashi for their kind assistance.

20) C. A. Coulson and C. Zauli, *Mol. Phys.*, **6**, 525 (1963); F. A. Gianturco and C. A. Coulson, *Mol. Phys.*, **14**, 223 (1968).
21) S. Oae and N. Kunieda, *Kagaku*, **20**, 581 (1965).