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Chemical-state Analysis by Means of Soft X-Ray Spectroscopy. II. *Kβ* Spectra for Phosphorus, Sulfur, and Chlorine in Various Compounds

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The phosphorus-, sulfur- and chlorine-*Kβ* spectra in various compounds are obtained by means of secondary excitation using a simple quasi-two-crystal X-ray spectrometer. The spectra thus obtained change depending upon the chemical state. The spectra are discussed from the point of view of chemical-state analysis. The spectral features are especially influenced by the hydrogen and oxygen of the ligand. The peak on the lower-energy side appears to be related to the oxygen, and the peak grows with an increase in the oxidation number. The spectrum gives information on the structural formula.

In previous paper[1,2] we have studied the $L_{2,3}$ emission spectra of phosphorus, sulfur, and chlorine in various compounds. As was noted earlier, the *Kβ* emission spectrum is related to the 3p character of the valence band. The $L_{2,3}$ emission spectrum, however, is sensitive to the 3s and 3d character of the valence band. Therefore, it is well known that the emission spectrum originating from electron transitions between the valence band and the inner shell provides a powerful technique for obtaining information about the electronic structure in the valence band or the chemical-bonding state.

The first evidence in a study of the *Kβ* emission spectra for phosphorus, sulfur, and chlorine compounds that X-ray spectra were influenced by the chemical combination was reported by Lindh and Lundquest,[3] who worked with direct electron bombardment. Following this discovery, very active investigations were begun to ascertain the effects of chemical combination on the X-ray spectra of many elements using a fluorescent-excitation technique. However, the effects of chemical combination on the X-ray spectra were found to be very slight except in the case of the light elements.

Recently, Takahashi *et al.*[4—6] obtained the *Kβ* spectra of phosphorus, sulfur, and chlorine compounds and discussed the *Kβ* spectral profile from the standpoint of chemical-state analysis. However, no sufficient discussion of the peak profile has yet been made because the spectrum is obtained with a single crystal spectrometer. A high-resolution spectrometer is necessary to observe fine splitting structures originating from chemical bonding, as the separation in the energy of the valence-band molecular orbitals is less than several electron volts. Gōshi[7] designed and constructed a simple two-crystal spectrometer in order to obtain highly energy resolved *Kβ* X-ray emission spectra and then applied it to chemical-state analysis. Whitehead[8] obtained the *Kβ* spectra of sulfur and chlorine compounds using a double-crystal X-ray spectrometer and discussed the spectra in terms of the molecular-orbital theory. Gōshi *et al.*,[9] in the latest date, constructed a wide-range two-crystal vacuum X-ray spectrometer and showed many possibilities in chemical shift measurement and chemical-state analysis.

There have been many experiments and studies of the *Kβ* spectra for the third-period elements in various compounds. However, no sufficient and systematic investigation of the *Kβ* spectra for these compounds, and no systematic studies of chemical-state analysis using these spectra, have yet been done. In this paper, a systematic investigation of the P-, S- and Cl *Kβ* spectra in various phosphorus, sulfur and chlorine compounds, and a discussion from the point of view of chemical-state analysis, will be done using a simple quasi-two-crystal spectrometer in order to obtain the high-resolution spectra. We have attempted to present the results of chemical-state analysis by means of soft X-ray spectroscopy in this and in companion papers;[10,11] also in this paper we will try to make clear the relationship between the character of the chemical state and the *Kβ* emission spectra.

Experimental

We designed and constructed a new, simple quasi-two-crystal spectrometer using a commercial single-crystal spectrometer. By rotating the detector arm at $3\Delta\theta$ relative to the rotation angle of the first crystal, (1) the analyzer wavelength can be obtained directly according to Bragg's diffraction law, $2d\sin\theta=n\lambda$, and (2) the scanning range satisfying Bragg's diffraction law is extended.

Figure 1 shows a schematic diagram of the quasi-two-crystal spectrometer in which a two-crystal attachement is added to a commercial single-crystal spectrometer. A parallel-foil collimator, A, limits the divergence of the X-

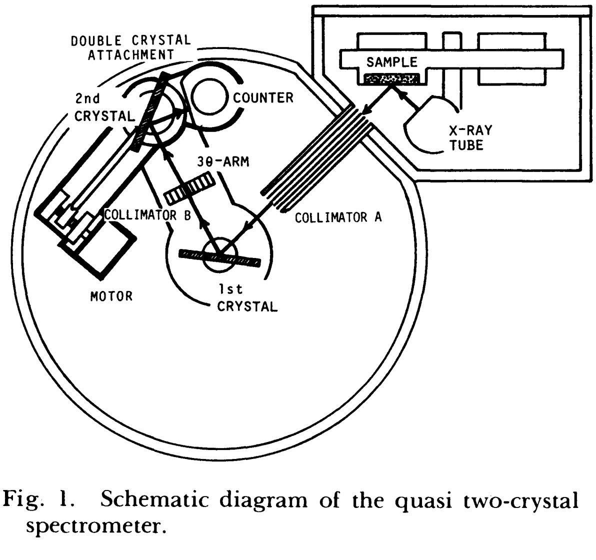


Fig. 1. Schematic diagram of the quasi two-crystal spectrometer.

rays incident on the first crystal, and the collimator, B, between the first- and second-crystals, limits the scattering of the X-rays. An attachment which includes the second crystal and a detector is coupled to the detector arm. The second crystal can be rotated by several degrees for fine adjustment using a bar driven through gears by a small motor. The collimator, A, is 10 cm long with 0.24 mm spacing and with a vertical 1 mm-spacing collimator attached. A flat Ge(110$\cdots$2d=6.532 Å) was used as an analyzer crystal. Background and impurity lines of a higher order can be reduced by using a gas-flow proportional counter with a pulse-height discriminator. P-10 gas is used as the counting gas and is sealed in the counter with a polycarbonate film window (6 μm thick). A Philips PW2188 chromium-target X-ray tube is used and operated at 50 kV and 50 mA. The primary characteristics of this spectrometer are: (1) the intensity and resolution are the same as those of an orthodox two-crystal spectrometer, and (2) it is easy to use and can easily be constructed. A detailed description of this spectrometer has been reported elsewhere.[12]

The solid specimens are prepared by pressing a fine powder into a smooth aluminum ring, thus keeping the target sample pure and at a constant pressure. The liquid samples are measured using a sample holder which is sealed with a polystyrene film window (15 μm thick). The spectrum is calibrated by the sharp Cu$K\beta$ line. In order to insure that the radiation-decomposition effect upon these measurements is negligible, the measurement has been done twice for each spectrum, using two identical samples. The total counting time is 30 s per point, and the counter is scanned, step by step, by 0.01 ° of 3θ.

Results and Discussion

In previous[1] and companion[10] papers, it has been shown that the $L_{2,3}$ fluorescence spectra of sulfate ions (SO_4^{2-}) reveal scarcely no influence of the cations of sulfate compounds. The same phenomenon is expected in the $K\beta$ fluorescence spectra. The S$K\beta$ emission spectra for Na_2SO_4, $CoSO_4$, $NaHSO_4$, $(NH_2)_2H_2SO_4$, and H_2SO_4 are shown in Fig. 2. In the ions of polyatomic compounds, the individual ionic groups, such as SO_4^{2-} in solid Na_2SO_4, K_2SO_4, or $CaSO_4$, are essentially isolated anions, as a whole, and are not signifcantly affected by the cations. In the $K\beta$ spectra from sulfate ions with a T_d symmetry, however, there are two main components. The T_d molecular symmetry has seven occupied orbitals (4a$_1$, 3t$_2$, 5a$_1$, 4t$_2$, 1e, 5t$_2$, and 1t$_1$) in the valence band. Hence, transitions into the 1s-level are allowed only from the t$_2$ orbital by the dipole-selection rule, and it seems that the main peak C, known as $K\beta_{1,3}$, should be a transition from the 4t$_2$ orbital, whose molecular orbital consists mainly of the 3p population of sulfur and the 2p population of oxygen. It seems that the position of the main peak C is not influenced by the kind of cation. If the cation of these compounds is replaced by hydrogen, however, the main peak C shifts just a little (≈1 eV). Because X-ray emission involves two levels, the chemical effect is the result of the shift of the core level also and of the structure of the valence band. The effect of the core-level shift is simply to shift the emission spectrum in terms of energy. Therefore, the spectral feature is related to the structure of the valence band. It seems reasonable that the main peak of the $K\beta$ spectra is not shifted by the shift of the core level 1s of sulfur in relation to hydrogen, because the 1s level of hydrogen is separated from the 1s level of sulfur; therefore, the molecular orbital in the valence band is affected in relation to hydrogen. The peak A, known as $K\beta'$ at a lower energy, should be identified as the 3t$_2$ orbital, whose molecular orbital consists mainly of the 3p population of sulfur and the 2s population of oxygen. It should be noted that the position of the peak A shows scarcely no influence of the cations; however, the peak A shifts just a little, like peak C, when the cation is replaced by hydrogen. The spectra can be expected to have one more component, as there is the 5t$_2$ molecular orbital in the valence band. That is the very small peak D, known as $K\beta''$, because the 5t$_2$ orbital consists of the 3d population of sulfur and the 2p population of oxygen. There is a small hump on the lower-energy side of the main peak C. This peak probably originates from the 5a$_1$ molecular orbital, whose molecular orbital consists mainly of the 3s population of sulfur and the 2s, 2p population of oxygen. If a symmetry of molecule is distorted and the 5a$_1$ molecular orbital contains the 3p population, an electron transition is allowed to the 1s level from 5a$_1$, with its 3p population, although transition into the 1s level is not allowed from the a$_1$ orbital by the dipole-selection rule. It thus seems that the peak B is influenced by the chemical bonding conditions and by the other cations.

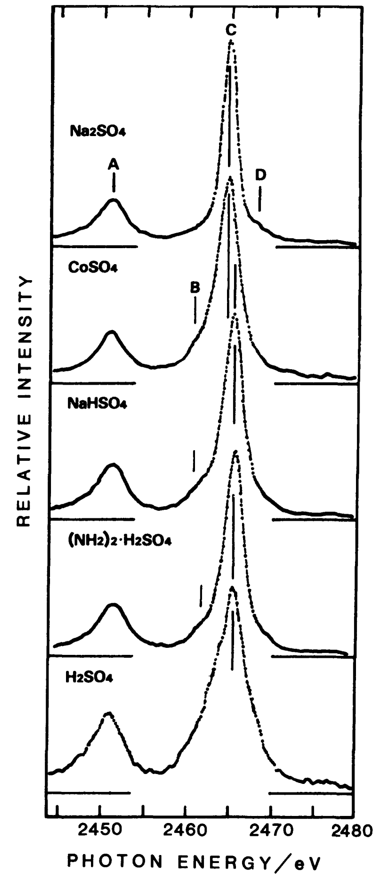


Fig. 2. Comparison of S$K\beta$ spectra of sulfate compounds.

The Cl$K\beta$ spectra for $LiClO_4$, $NaClO_4$, and $KClO_4$ are shown in Fig. 3. It should be noted that the $K\beta$

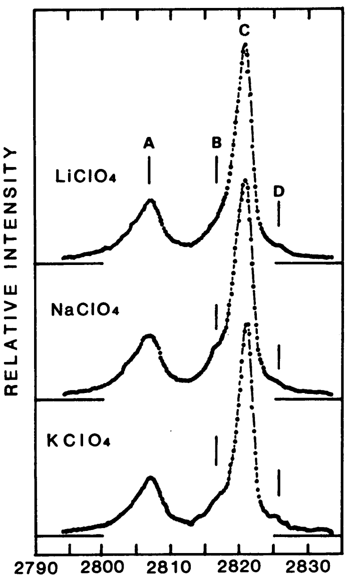


Fig. 3. Comparison of Cl$K\beta$ spectra of perchlorate compounds.

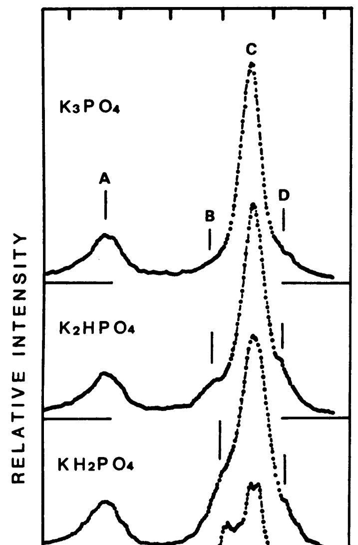
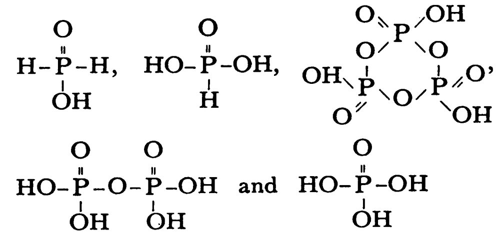


Fig. 4. Comparison of P$K\beta$ spectra of potassium phosphates and phosphoric acid.

spectral profiles of perchlorate ions reveal scarcely no influence of the cation, except for the hump B. The hump B grows up in proportion to the increase in the atomic number of the cation. It seems that the hump B originates from the electron transition from the 5a$_1$ molecular orbital of the distorted T$_d$ symmetry to the 1s level, and that the molecular orbital is affected by the interaction between the anion and the cation. If the covalent interaction between the ions is relatively small, it seems that hump B becomes negligibly small.

The P$K\beta$ spectra for K_3PO_4, K_2HPO_4, KH_2PO_4, and H_3PO_4 in each of which the metallic cation is replaced by hydrogen, are compared in Fig. 4. The covalent interaction between PO_4^{3-} and the cations of these compounds is relatively large except in the case of H_3PO_4. No hump B appears in the spectrum in the case of K_3PO_4, but the hump B appears and grows in the cases of K_2HPO_4 and KH_2PO_4, and the hump B grows into a large peak in the case of H_3PO_4. Moreover, the hump B shifts to the higher-energy side according to the contribution of hydrogen. It seems that hydrogen contributes to the hump B and that the intensity of the hump B increases according to the increase in the covalent interaction between the anion and the cation. The main peak C shifts just a little in relation to the hydrogen atom. There is a small component D on the higher-energy side of the main peak.

For a consideration of the contributions of the hydrogen ion or the hydroxide ion in the $K\beta$ spectrum, the P$K\beta$ spectra for phosphinic acid (HPH_2O_2), phosphonic acid (H_2PHO_3), *cyclo*-triphosphoric acid ($H_3P_3O_9$), and pyrophoshoric acid ($H_4P_2O_7$) are compared in Fig. 5. The measured spectra change depending upon the chemical state. The spectra of HPH_2O_2 and H_2PHO_3 have hump B, while $H_3P_3O_9$, $H_4P_2O_7$, and H_3PO_4 have peak B, which is clearly separated from the main peak C. The structural formulas for HPH_2O_2, H_2PHO_3, $H_3P_3O_9$, $H_4P_2O_7$, and H_3PO_4 are:



$$\text{H-}\underset{\text{OH}}{\overset{\text{O}}{\text{P}}}\text{-H},\quad \text{HO-}\underset{\text{H}}{\overset{\text{O}}{\text{P}}}\text{-OH},$$

$$\text{HO-}\underset{\text{OH}}{\overset{\text{O}}{\text{P}}}\text{-O-}\underset{\text{OH}}{\overset{\text{O}}{\text{P}}}\text{-OH} \quad \text{and} \quad \text{HO-}\underset{\text{OH}}{\overset{\text{O}}{\text{P}}}\text{-OH}$$

respectively. In the structural formula of HPH_2O_2 or H_2PHO_3, the central P atom combines with O, OH, and H. However, in the case of $H_3P_3O_9$, $H_4P_2O_7$, or H_3PO_4, the central P atom combines with O and OH. In these cases, the $K\beta$ spectral features for these compounds have something in common with each other. However, in the case of the O$K\alpha$ spectrum for these compounds, the spectral features change.[11] It seems reasonable to consider that those spectral features are influenced by the conditions of the surrounding atoms for the observed atom, not by the difference in structure formulas. The same conclusion can be observed for the $L_{2,3}$ emission spectra.[2]

In a companion paper,[10] it will be shown that the main peak of the $L_{2,3}$ emission spectra shifts to the higher-energy side with the increase in the oxidation number. The same phenomenon is observed in the $K\beta$ spectra of oxide compounds. Figure 6 compares the Cl$K\beta$ spectra for NaCl, NaClO, $NaClO_2$, $NaClO_3$, and $NaClO_4$. These spectra change corresponding to the chemical-bond state and also with the number of bonding oxygen atoms. These spectra have fine structures depending upon the chemical state. The main peak C and the small peak D on the higher-energy side shift to higher energy side, but the peak A on the lower-energy side only shifts a little, to higher energy side with the increase in the oxidation number. If

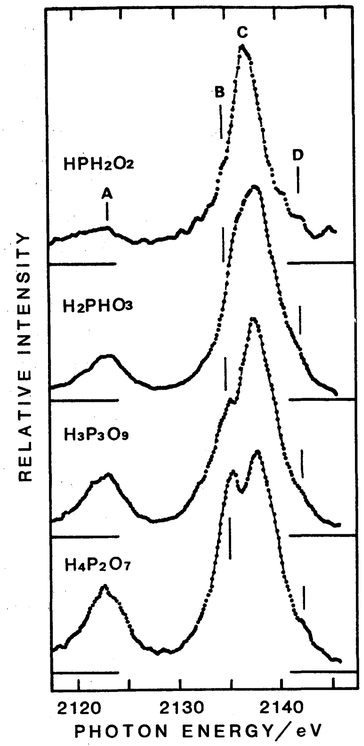


Fig. 5. Comparison of P$K\beta$ spectra of phosphinic acid, phosphonic acid, *cyclo*-triphosphoric acid, and pyrophosphoric acid.

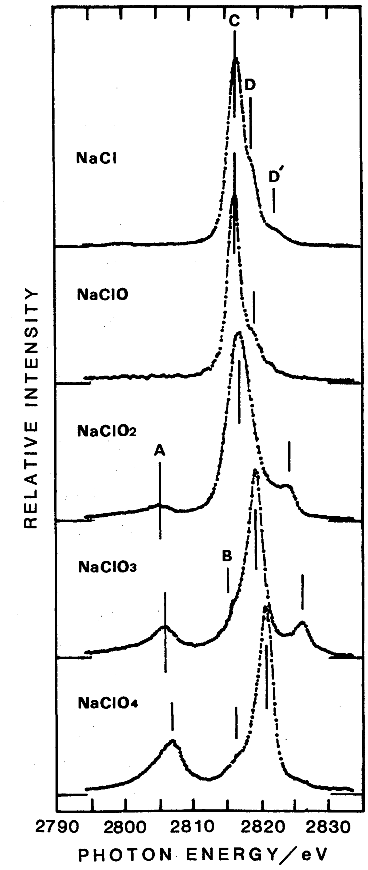


Fig. 6. Comparison of Cl$K\beta$ spectra of NaCl, NaClO, $NaClO_2$, $NaClO_3$, and $NaClO_4$ which are different in the bonding oxygen atom number.

NaCl is of a perfect ionic bond, one can expect that the spectrum will consist of only one component, because there is only the 3p level of the Cl ion which is allowed the transition to the inner ls level. However, the spectrum of NaCl has three components. It seems reasonable to say, therefore, that NaCl involves a partial covalent character. The peak A originates from the transition from the molecular orbitals which consist mainly of the Cl-3p and O-2s populations. Therefore, the peak A grows in proportion to the increase in the number of oxygen. The peak D originates from the transition from the molecular orbitals which consist mainly of the O-2p population, but the molecular orbital involves the Cl-3p or Cl-3d population a little. In the case of ClO_4^-, the peak D is negligibly small, because the ClO_4^- has the oxygen lone pair orbital. However, the peak B on the lower-energy side of the main peak seems to grow with the increase in the oxidation number.

A similar example of the sulfur $K\beta$ spectra for $Na_2S_2O_4$, $Na_2S_2O_5$, $Na_2S_2O_6$, and $Na_2S_2O_7$ is shown in Fig. 7. These spectra consist of five peaks, and they show differences in the chemical-bond state as a function of the number of bonding oxygen atoms. Each peak shifts to the higher-energy side with an increase in the number of oxygen atoms. This fact can be thought to indicate that the initial level (core vacancy) for the electron transition shifts to the higher-energy side according to the increase in the quantity of oxygens combined with the sulfur atom. While the peak A develops with the oxygen atoms, the peak E decays,

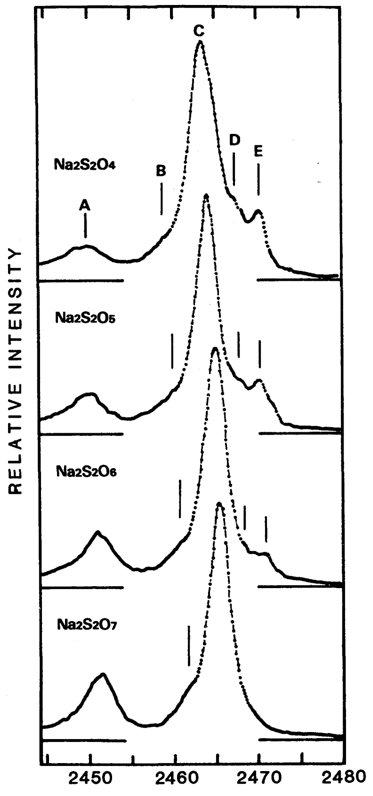
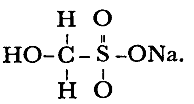


Fig. 7. Comparison of S$K\beta$ spectra of $Na_2S_2O_4$, $Na_2S_2O_5$, $Na_2S_2O_6$, and $Na_2S_2O_7$ which are different in the bonding oxygen atom number.

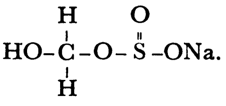
and it is barely seen in the $Na_2S_2O_7$ spectrum. The peak D is clearly observed in either $Na_2S_2O_4$ or $Na_2S_2O_5$, but not in $Na_2S_2O_6$ or $Na_2S_2O_7$, while in the case of the peak B, the opposite behavior is seen.

We should like to demonstrate another case of the relation between the *Kβ* spectrum and the chemical-bond-state conditions. Figure 8 shows a comparison of the sulfur *Kβ* spectra for sodium benzenesulfinate ($C_6H_5SO_2Na$), sodium sulfate (Na_2SO_3), sodium hydrogensulfite ($NaHSO_3$), sodium hydroxymethanesulfinate ($HOCH_2SO_2Na$), and sodium hydroxymethanesulfinate ($HOCH_2SO_3Na$). These compounds contain mainly three or four components in the *Kβ* spectra. It seems that these spectra all show similar features, but differ from the spectrum of sulfate compounds. However, the intensity ratio of the spectral components of these compounds changes with the chemical state. These compounds contain the $-CSO_2-$ or $-SO_3-$ in their structural formulas. It seems that the main peak B reveals scarcely no influence of the chemical state. However, the peaks A and C change with the chemical state, and it seems that the intensity of the peak C decreases and the position of the peak C shifts to the higher-energy side according to the increase in the peak A. In the case of $NaHSO_4$ in Fig. 2, the small peak B which is contributed by the hydrogen atom appears on the lower-energy side of the main peak of the S*Kβ* spectra. From these considerations, it seems reasonable that the small peak D of $NaHSO_3$, $HOCH_2SO_3Na$ and $HOCH_2SO_2Na$ is related to the hydrogen atom. In Ref. 5, it is supposed, from an X-ray spectral analysis, that the structural formula for $HOCH_2SO_3Na$ is a sulfone-type structure:



$$HO-\overset{H}{\underset{H}{C}}-\overset{O}{\underset{O}{S}}-ONa.$$

If this conclusion is true, the spectrum of $HOCH_2SO_3Na$ should be classified in the sulfate (SO_4^{2-}) group, as the 2p electrons of carbon play the same role in the valence band as the 2p electron of oxygen in combination with sulfur. However, the spectral profile of $HOCH_2SO_3Na$ seems to be classifiable in the sulfite (SO_3^{2-}) group. Our spectrum analysis suggests that the structural formula for $HOCH_2SO_3Na$ should be given as follows:



$$HO-\overset{H}{\underset{H}{C}}-O-\overset{O}{S}-ONa.$$

The lowest-energy peak originates from the electron transition from the molecular orbital which consists mainly of the 3p population of sulfur and the 2s population of oxygen. Therefore, if it is no contributed with oxygen atoms, the peak A should not be in the *Kβ* spectra. The S*Kβ* spectra for sulfur compounds which contain thiourea or other such substances, but do not contain the oxygen atom, are shown in Fig. 9. These compounds contain mainly two components. The main peak B reveals scarcely no influence, but the intensity and position of peak A are affected by the chemical state. The structural formula for the com-

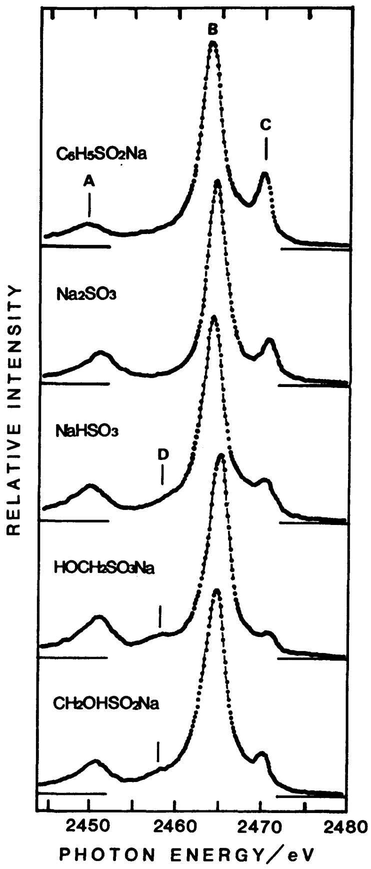


Fig. 8. Comparison of S*Kβ* spectra of sodium benzenesulfinate, sodium sulfate, sodium hydorgensulfite, sodium hydroxymethanesulfinate, and sodium hydroxymethanesulfonate.

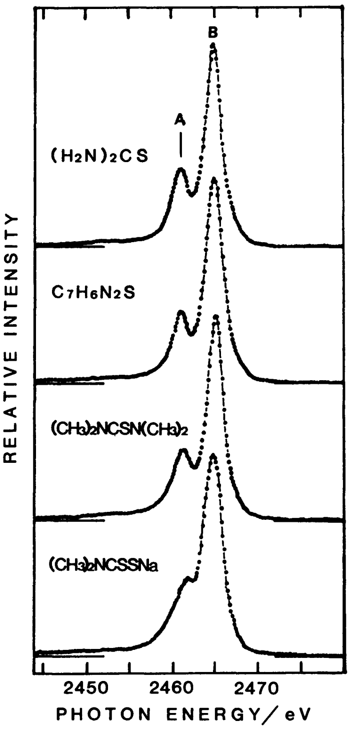
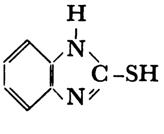
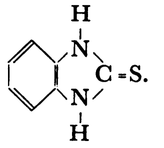


Fig. 9. Comparision of S*Kβ* spectra of thiourea, 2-mercaptobenzimidazole, tetramethylthiourea, and sodium dimethyldithiocarbamate which do not contain oxygen.

pounds of thiourea has a double bond of carbon and sulfur. The two structural formulas in 2-mercaptobenzimidazole ($C_7H_6N_2S$) may be given as the follows:



and



I II

However, in comparing the spectra, it seems reasonable to say that the structural formula for ($C_7H_6N_2S$) has a thiocarbonyl form II. This conclusion is the same as that is given in Ref. 5.

Finally, the Cl*Kβ* emission spectra of HCl, LiCl, NaCl,and KCl are shown in Fig. 10 in order to consider the relation of the ionic bond and the covalent bond with the *Kβ* X-ray spectra. These spectra have satellite peaks depending upon the chemical state. Therefore, it should be noted that these compounds have a partial covalent character and that the Cl*Kβ* spectrum is affected by the kind of cation. If these compounds have a highly ionic bond, these spectra can be expected to have only one peak component, originating from the 3p atomic level. However, one can not discuss the ionic and covalent characters of these compounds from their *Kβ* spectra alone. Although each peak shifts a little to the higher-energy side according to the atomic-number-increase order: Li, Na, and K, in the Cl $L_{2,3}$ emission spectra, the main peak in the case of the *Kβ* spectra reveals scarcely no influence of the cations.

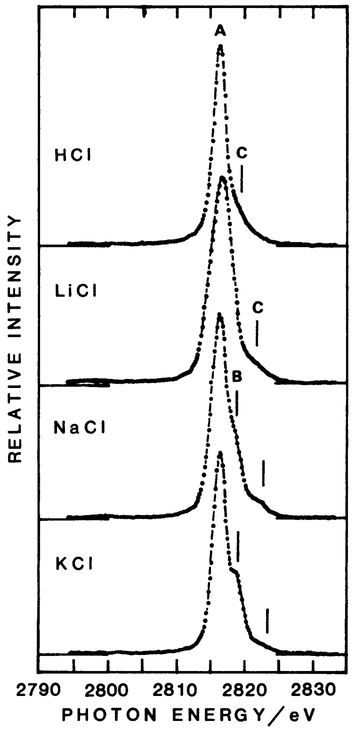


Fig. 10. Comparison of the Cl*Kβ* spectra of HCl, LiCl, NaCl, and KCl which combine with different cations.

Conclusion

In this paper, we constructed a simple two-crystal spectrometer and showed, using it, that spectra taken with a high resolution spectrometer can give us not only important information for studies of molecular orbitals, but also useful information for application to chemical-state analysis.

We have found the following properties:

(1) Although the $L_{2,3}$ emission spectra of the highly ionic bond reveal scarcely no influence of the cations,[10] the *Kβ* spectra for phosphorus, sulfur, and chlorine in various compounds are affected by the kind of cation.

(2) The *Kβ* spectra for the different central atoms of compounds which have T_d molecular symmetry show features similar, as with the $L_{2,3}$ emission spectra.

(3) A peak related to the hydrogen or hydroxyl group is observed on the lower-energy side of the main peak, except in the case of HCl. It seems that the X-ray emission spectra give information about the contribution of hydrogen.

(4) The each peak of the *Kβ* spectra shifts to the higher-energy side with an increase in the oxidation number.

(5) As the spectral features are sensitive to the chemical condition of the surrounding atoms, one can consider and decide the structural formula from a comparison of the spectra.

In this work, we can not interpret the spectra by the help of a molecular-orbital calculation and can not discuss the spectra quantitatively. This must remain a subject for future study.

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