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Chemical-state Analysis by Means of Soft X-Ray Spectroscopy. I. $L_{2,3}$-Emission Spectra for Phosphorus, Sulfur, and Chlorine in Various Compounds

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The phosphorus-, sulfur-, and chlorine-$L_{2,3}$ emission spectra in various compounds are obtained using secondary excitation. The spectra are discussed from the point of view of chemical-state analysis. It should be noted that the spectra of a highly ionic bond reveal scarcely no influence of the cations. However, the spectra with a covalent character are complex as a result of the molecular orbital generated with the covalent bond. The spectral features are influenced by the chemical condition of the surrounding atoms and are sensitive to oxygen and hydrogen.

X-Ray spectroscopy has long been a basic method for studying the elemental compositions of materials and the electronic structures of atoms. It has been known since the 1920's that the X-ray emission spectrum of an element varies according to the state of its chemical combination. However, the effect of chemical combinations on X-ray spectra has been found to be very slight except in the case of a light element. In an earlier work, Lindh and Lundquist[1] were able to observe the chemical-combination effect of X-ray spectra in their studies of the $K\beta$ emission spectra of phosphorus, sulfur, and chlorine compounds. The problems encountered by earlier investigators in X-ray emission spectroscopy were generated mainly by the highly energetic conditions of the direct-electron bombardment of the sample deposited on the anticathode of the X-ray tube. This type of excitation leads to sample oxidation, reduction, decomposition, and other reactions with the anticathode material, which thereby generate a variety of products which add to the complexity to the observed spectra.

The twenty-year period between 1930 and 1950 there were fluorescence X-ray investigations of the $K\beta$ spectra from the point of view of the chemical-state analysis of sulfur, chlorine, and phosphorus in various compounds. The results of these investigations also showed that the effect of chemical bonding had very little influence on an X-ray spectrum.

As was noted earlier,[2] the $K\beta$ emission spectrum is related to the 3p character in the valence band. However, the $L_{2,3}$ emission spectrum is sensitive to the 3s and 3d character of the valence band. For an isolated phosphorus, sulfur, or chlorine in its ground state, the valence-band electrons tend to remain in the 3s and 3p character. In chemical combination, however, some of these valence-band electrons may be partially involved, to a greater or lesser extent, in the 3d orbital and may thereby enhance the 3d character of the molecular orbital structure. In the $L_{2,3}$ emission spectra, therefore, the chemical effect is more extensitive than in the $K\beta$ emission spectra.

Henke and Smith[3] were able to demonstrate the feasibility of obtaining the $L_{2,3}$ spectra of phosphorus, sulfur, and chlorine in various compounds by applying spectrographic techniques of such efficiency as to minimize the effects of radiation decomposition. The $L_{2,3}$ emission spectra of sulfur and chlorine in several compounds have since been more precisely measured and studied from the point of view of the molecular orbital.[2,4–6] However, no sufficiently systematic investigation of the $L_{2,3}$ emission spectra of phosphorus, sulfur, and chlorine in various compounds has been made.

We attempt to describe a chemical-state analysis by means of soft X-ray spectroscopy in this and in companion papers;[7,8] also, in this paper we will try to make clear the relationship between the character of the chemical state and the $L_{2,3}$ emissiom spectra.

Experimental

The high-efficiency techniques which have been developed by Henke *et al.*[9,10] for the secondary excitation of ultrasoft X-ray spectra have made possible the interpretation of the valence-band X-ray spectra for the light element. Ultrasoft X-ray excitation greatly reduces the radiation damage to samples and provides a considerably improved peak-to-background ratio. The basic spectrographic approach that was used in this laboratory is shown in Fig. 1. The X-ray spectrometer is of a vacuum X-ray type provided with a Soller collimator (0.3 mm spacing, 100 mm length). After reflection from the plane crystal, the beam

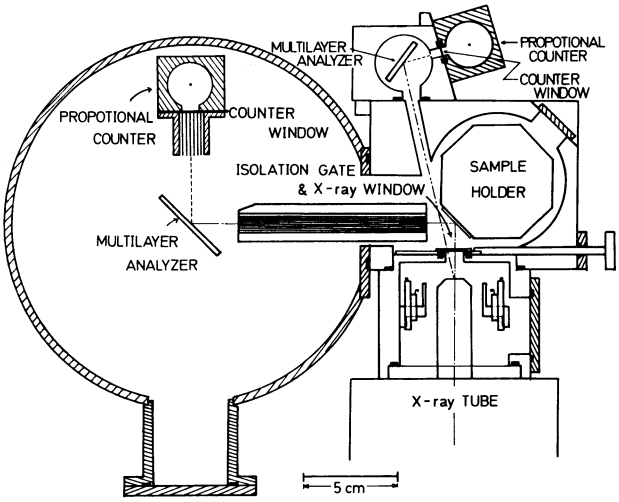


Fig. 1. A single-crystal spectrographic approach for low energy X-ray spectroscopy applying closely coupled demountable X-ray source, the development of large-soap-film crystals, and tuned subatmospheric pressure.

from the fluorescent radiator passes through the Soller collimator (1.0 mm spacing, 20 mm length) before the counter. The most intense and practical line source in the $L_{2,3}$ of phosphorus, sulfur or chlorine is $CK\alpha$ (44.6 Å). It is generated in our demountable source using a copper anode coated with a colloidal graphite. The source is stable for many hours of operation, typically at 8 kV and 150 mA. The X-ray tube window is constructed with a polycarbonate film (Kimfoil) with an aluminum coating a few hundred angstrom thick which has an effective transmission band for the carbon $K\alpha$ (44.6 Å) radiation.

The plane crystal is a specially developed Langmuir-Blodgett-type multilayer[11] analyzer, of lead stearate for chlorine and sulfur compounds or of lead lignocerate for phosphorus compounds, which has $2d$-spacing of 100 Å or 130 Å respectively. Background and impurity lines of a higher order can be reduced by using a gas-flow proportional counter with a pulse-height discriminator. Propane gas at a pressure of 60 mmHg (1 mmHg ≈133.322 Pa) is used as a counting gas and is sealed in the counter with poly(vinyl formal) film (Formver). The solid specimens are prepared by pressing a fine powder into a smooth aluminum ring in order to keep the target sample pure and at a constant pressure. The liquid samples are measured under freezing conditions using the cryostat shown in Fig.2. The spectrum is calibrated by the sharp $M\zeta$ lines of zirconium (81.9 Å) and molybdenum (64.5 Å). A detailed description of these experimental techniques has been reported elsewhere.[10] In order to insure that the radiation decomposition effect upon these measurements would be negligible, the measurement has been done twice for each spectrum with two identical samples. The total counting time is 50 s per point, and the counter is scanned step by step, by 1/10 s or 2/10 degree.

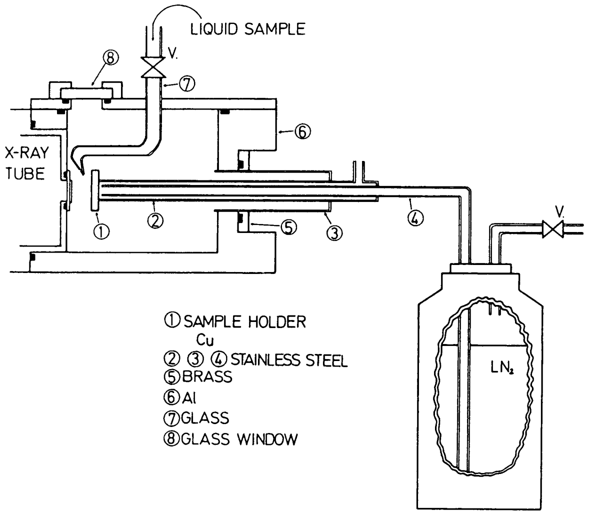


Fig. 2. Sketch of the cryostat for sample holder. The liquid samples were measured at the freezing conditions using the cryostat controlled by liquid nitrogen.

Figure 3 shows schematically a flow- and pressure-regulated system for the counter, and vacuum systems for the sample chamber and the X-ray tube. The optimum pressure in the counter (P.C.) is maintained by the controls with valves (V1 and V2). The gas pressure is indicated by the gauges (P.G.) and the manometer (U.M.M.). The gas is allowed to flow through the flow meter (F.M.) at a rate of 50 cm³/min. The V3 valve is usually closed, but it is opened in order to keep the same pressure in the counter and the spectrometer when the spectrometer is pumped down to a vacuum from the atmosphere. The spectrometer and the sample chamber are pumped to about 10^{-3}'s Torr (1 Torr≈ 33.322 Pa) by means of a rotary pump. The X-ray tube is pumped to about 10^{-6}'s Torr by means of a diffusion pump and rotary pump.

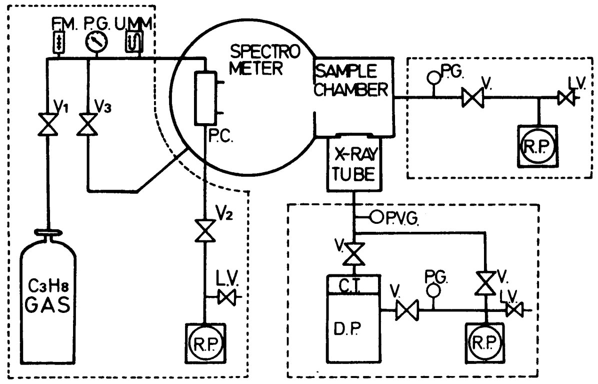


Fig. 3. Schematic diagram of the flow and pressure regulated system for the counter, and vacuum systems for the sample chamber and the X-ray tube.

Results and Discussion

In a previous paper,[2] our studies of the sulfur $L_{2,3}$ emission spectra and molecular orbital studies of sulfur compounds were reported. In that paper, the $L_{2,3}$ fluorescence spectra of sulfate ions (SO_4^{2-}) reveal scarcely no influence of the cations of these sulfate compounds. In the case of perchlorate ions (ClO_4^-), the same phenomenon is observed in the $L_{2,3}$ fluorescence spectra. Cl $L_{2,3}$ emission spectra for $LiClO_4$, $NaClO_4$, $KClO_4$, and $AgClO_4$ are shown in Fig. 4. It should be noted that the $L_{2,3}$ fluorescence spectra of perchlorate ions reveal scarcely no influence of the

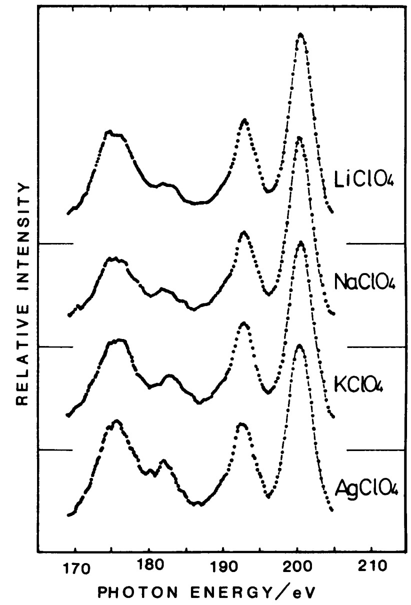


Fig. 4. Chlorine-$L_{2,3}$ emission spectra for $LiClO_4$, $NaClO_4$, $KClO_4$, and $AgClO_4$. Chlorine-$L_{2,3}$ emission spectra have been excited by $CK\alpha$ radiation and analyzed by lead stearate.

cations. This reflects the fact that the covalent interaction between the ions is relatively small, thus accounting for the narrow emission bands, which can be attributed either to the cations or to the anions. With this evidence for strong localization, it seems reasonable to suggest that the crystal effect should be neglected.

In general, there is a similarity in features of the $L_{2,3}$ emission spectra between the molecules with different central atoms, but all with the T_d symmetry, although the energy ranges of the emission spectra are different. A comparison of the features of the $L_{2,3}$ emission spectra for the central atom of the T_d symmetry with Li_3PO_4, Li_2SO_4, and $LiClO_4$ is shown in Fig. 5. There are seven occupied orbitals ($4a_1$, $3t_2$, $5a_1$, $4t_2$, 1e, $5t_2$, and $1t_1$) in the valence band for these examples of T_d molecular symmetry. Hence, transitions into the 2p-level are allowed only from the a_1, t_1, and e orbitals by the dipole-selection rule. The peaks at lower energy and a middle energy should be assigned to $4a_1$ and $5a_1$ respectively, whose molecular orbitals consist mainly of the 3s population. The main peak at a higher energy has to be assigned to the 1e and $5t_2$ orbitals with then comparatively high 3d population. The intensity ratios of the peak at a middle energy (from $5a_1$) and at a higher energy ($1e+5t_2$) increase with the increase in the atomic number of X for the XO_4^{2-} cluster. It seems reasonable that the 3d population in the valence band increases with a increase in the atomic number of X; therefore, the peak at a higher energy, which is assigned to the 1e and $5t_2$ orbitals, with then comparatively high 3d population, will increase. In the $LiClO_4$, a small peak appears between $4a_1$ and $5a_1$. This peak should be assigned to $3t_2$, where molecular orbital consists mainly of the 3p and 3d populations of Cl and the 2s population of O. The electron transition involves two excited states, and, as the initial vacancy (core level) has two possible states, $2p_{1/2}$ (L_{II}) and $2p_{3/2}$ (L_{III}), corresponding to the $2p^5$ configuration, the emission component which is due to a transition from a molecular orbital to the 2p levels will result in two emission lines. This spin-orbit separation, however, is about 1.2 eV, and the energy resolution of the spectrometer is about 1 eV for this wavelength region. Therefore, the emission spectra can reflect the structure of the molecular orbital, as the spin-doublet effect need not be so considered.

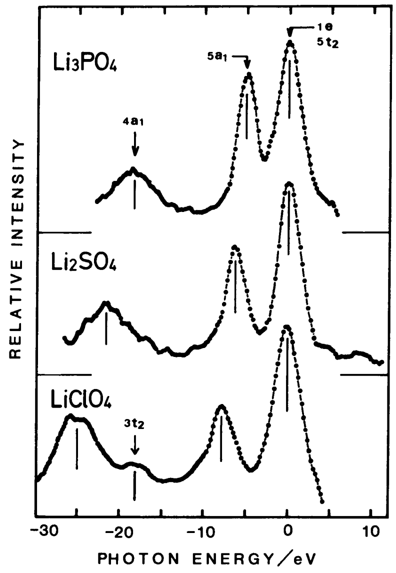


Fig. 5. Comparison of the feature of the $L_{2,3}$ emission spectra of the central atoms of T_d symmetry for Li_3PO_4, Li_2SO_4, and $LiClO_4$. Also shown are the positions of peaks and the molecular orbital assignment for each peak.

The phosphorus $L_{2,3}$ fluorescence spectra of Li_3PO_4, K_3PO_4, KH_2PO_4, and H_3PO_4, all of which are composed of the phosphate ion (PO_4^{3-}), are shown in Fig. 6. In this figure, the spectrum of H_3PO_4 differs from that of another phosphate especially in the middle-energy range, though the peak positions on the lower-energy side and the higher-energy side are quite the same. The phosphate anion for strong localization

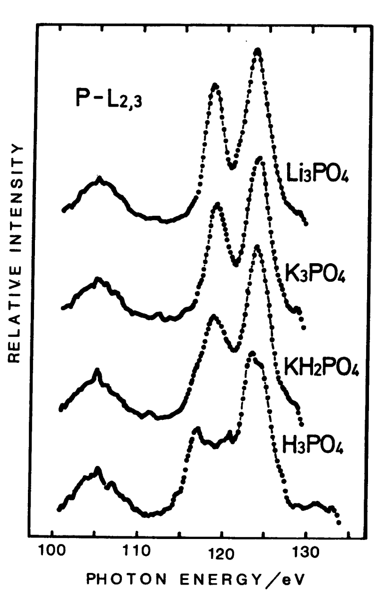


Fig. 6. Comparison of the phosphorus-$L_{2,3}$ emission spectra. Phosphorus-$L_{2,3}$ emission spectra have been excited by C$K\alpha$ radiation and analyzed by lead lignocerate.

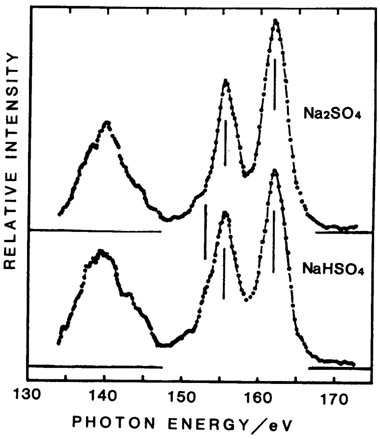


Fig. 7. Sulfur-$L_{2,3}$ emission spectra for Na_2SO_4 and $NaHSO_4$. Sulfur-$L_{2,3}$ emission spectra have been excited by C$K\alpha$ radiation and analyzed by lead stearate.

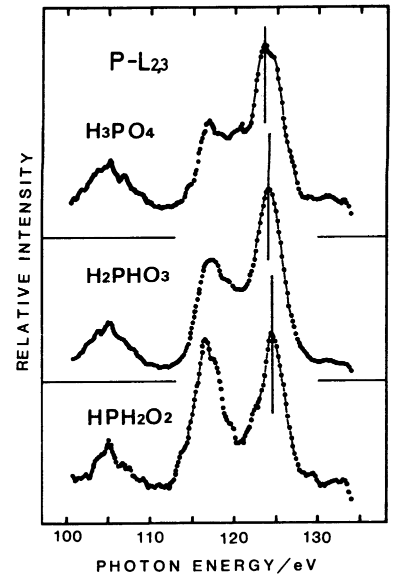
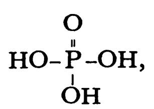
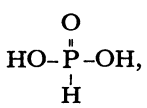


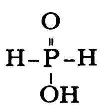
Fig. 8. Comparison of the phosphorus-$L_{2,3}$ emission spectra for phosphoric acid, phosphonic acid, and phosphinic acid. Phosphorus-$L_{2,3}$ emission spectra have been excited by C$K\alpha$ radiation and analyzed by lead lignocerate.

has a tetrahedral symmetry (T_d point group). However, the phosphate anion of H_3PO_4 does not have tetrahedral symmetry because there is not strong localization between PO_4^{3-} and the three H^+. Therefore, in view of the three hydrogens, it seems reasonable that H_3PO_4 has molecular symmetry. If Fig. 6 is looked at carefully, it can be found that the spectral feature of KH_2PO_4 differ just a little from those of other phosphate compounds. The same phenomenon is observed in sulfur compounds. Figure 7 shows a comparison of the sulfur $L_{2,3}$ emission spectra for Na_2SO_4 and $NaHSO_4$. In this case also, there is a hump on the low-energy side of the middle peak in $NaHSO_4$. This may reflect the fact that the structure of the valence band molecular orbital is affected by the H-atom contribution. These facts may suggest that X-ray emission spectra can give information about the chemical bonding of hydrogen; if so, this would be very important.

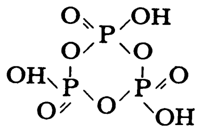
The P $L_{2,3}$ emission spectra for phosphoric acid (H_3PO_4), phosphonic acid (H_2PHO_3), and phosphinic acid (HPH_2O_2), are compared in Fig. 8. Each spectrum consists of three major peaks, at about 105, 117, and 124 eV. The measured spectra difference depends upon the chemical state. In proportion to the decrease in the number of oxygen atoms, the peak at about 124 eV shifts to the higher-energy side just a little and the peak at about 117 eV increases. The structural formulas for H_3PO_4, H_2PHO_3, and HPH_2O_2 are:


$\mathrm{HO}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{OH}}{|}}{\mathrm{P}}}-\mathrm{OH}$,

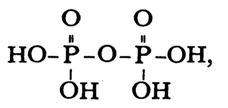

$\mathrm{HO}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{P}}}-\mathrm{OH}$, and


$\mathrm{H}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{OH}}{|}}{\mathrm{P}}}-\mathrm{H}$

respectively. In the structural formula of H_3PO_4, the central P atom combines with O atoms only. In the H_2PHO_3, the central P atom combines with three O atoms and one H atom. In the HPH_2O_2, however, the central P atom combines with two O atoms and two H atoms. The peak at about 117 eV increases corresponding to the number of direct combinations of the H atom to the P atom. On the other hand, the structural formulas for *cyclo*-triphosphoric acid ($H_3P_3O_9$) and pyrophosphoric acid ($H_4P_2O_7$) are:



and


$\mathrm{HO}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{OH}}{|}}{\mathrm{P}}}-\mathrm{O}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{OH}}{|}}{\mathrm{P}}}-\mathrm{OH}$,

respectively; here, the central P atom combines directly with the O atom, like only H_3PO_4. In this case, the spectral features of these compounds have something in common (Fig. 9). It seems reasonable to consider that the spectral features of these compounds are influenced by the surrounding atoms, but not by the bond conditions.

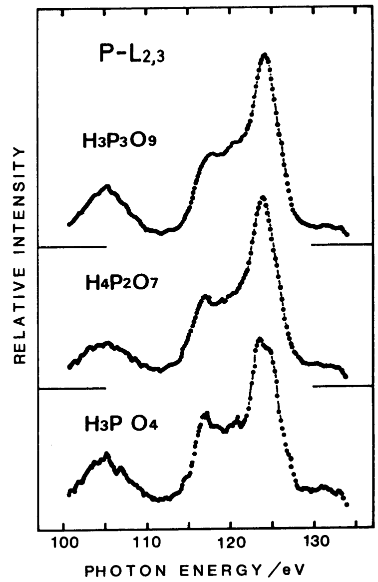


Fig. 9. Comparison of the phosphorus-$L_{2,3}$ emission spectra for phosphoric acid, *cyclo*-triphosphoric acid, and pyrophosphoric acid. Phosphorus-$L_{2,3}$ emission spectra have been excited by C$K\alpha$ radiation and analyzed by lead lignocerate.

The relation between the number of oxygen atoms and the spectral features will be considered. The Cl $L_{2,3}$ emission spectra of NaCl, $NaClO_2$, $NaClO_3$, and $NaClO_4$ are shown in Fig. 10. It is shown that the main peak of the $L_{2,3}$ emission spectra shifts to the higher-energy side and decreases with the increase in the oxidation number. The peak of the higher-energy side appears, and then increases in proportion to the increase in the number of oxygens. It is reasonable to think that the Cl-3d atomic orbital population increases in the valence band according to the increase in the number of oxygens combined to the chlorine atom. Thus, it is found that the 3d atomic orbital plays a very important role in the molecular orbital for the chemical combination of chlorine and oxygens.

Figure 11 shows a comparison of the sulfur $L_{2,3}$ emission spectra for $Na_2S_2O_4$, $Na_2S_2O_5$, $Na_2S_2O_6$, and $Na_2S_2O_7$. These spectra change corresponding to the

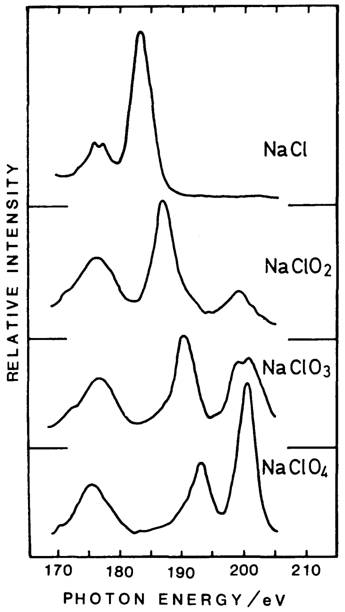


Fig. 10. Chlorine-$L_{2,3}$ emission spectra for NaCl, $NaClO_2$, $NaClO_3$, and $NaClO_4$. Chlorine-$L_{2,3}$ emission spectra have been excited by C$K\alpha$ radiation and analyzed by lead stearate.

chemical-bond state and also with the bonding O atom number. It can thus be thought that the existence of the oxygen atom makes the molecular orbital of the valence band attracted to the O-2p level. In Fig. 11, in proportion to the increase in the quantity of oxygen, the middle peak shifts to the higher-energy side and decreases just a little, while the peak of the higher-energy side increases and shifts just a little to the higher-energy side, but the peak of the lower-energy side does not show any influence of the quantity of oxygen.

Finally, the Cl $L_{2,3}$ emission spectra of LiCl, NaCl, KCl, and AgCl are shown in Fig. 12 in order to make possible a consideration of the relation of the ionic bond and covalent bond to the X-ray spectra. Since these compounds all have highly ionic bonds except for AgCl, the $L_{2,3}$ spectra of these compounds can be expected to be due to the electon transition from the M_1 level to the $L_{2,3}$ levels. However, these spectra have mainly two peak components. Each peak shifts just a little to the higher-energy side according to the order of the increase in the atomic number: Li, Na, and K, but it shifts to the lower-energy side for Ag. The differences in electronegativity between the cation and the anion of the molecule are 2, 2.1, 2.2, and 1.1 for LiCl, NaCl, KCl,and AgCl respectively. Therefore, it seems reasonable that the spectral peaks shift to the higher-energy side with the increase in the ionic character. If these compounds have a highly ionic bond, only the major components in the $L_{2,3}$ spectrum can be expected to fill the $L_{2,3}$ core from the M_1 level. Therefore, it is reasonable to think that the most intense peak is due to the transition from M_1 to $L_{2,3}$.

Cooper and Lavilla[12] interpreted the lower-energy peak in the spectrum of argon as a '*semi-Auger*' process in the $L_{2,3}$ emission, which is a '*shake-up*' process accompanied by the X-ray emission. The final state of the X-ray emission can be mixed strongly with states where one of the $M_{2,3}$ electrons is removed and the other is excited, provided that these levels have the same parity. A similar satellite structure is observed in the XPS spectra of argon and alkali halides.[13] A study of the Cl $L_{2,3}$ spectrum clearly indicates that the low-energy tail is due to a series of transitions of this type. The small peak is observed at the higher-energy side in AgCl; this may reflect the fact that this peak is due to a

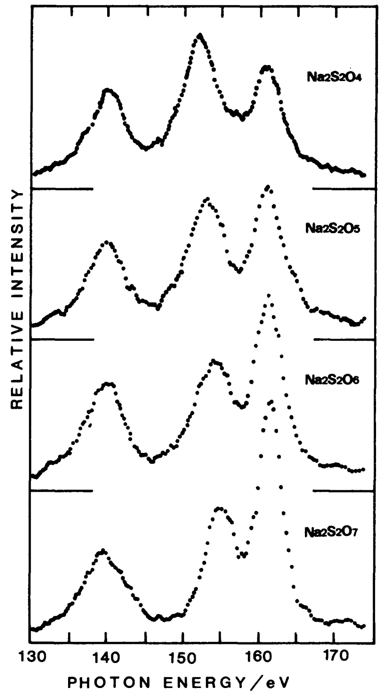


Fig. 11. Sulfur-$L_{2,3}$ emission spectra for $Na_2S_2O_4$, $Na_2S_2O_5$, $Na_2S_2O_6$, and $Na_2S_2O_7$. Sulfur-$L_{2,3}$ emission spectra have been excited by C$K\alpha$ radiation and analyzed by lead stearate.

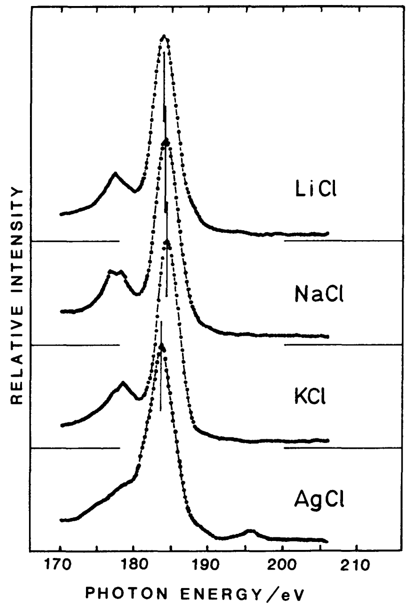


Fig. 12. Chlorine-$L_{2,3}$ emission spectra for LiCl, NaCl, KCl, and AgCl. Chlorine-$L_{2,3}$ emission spectra have been excited by C$K\alpha$ radiation and analyzed by lead stearate.

transition from a molecular orbital in the valence band to the $L_{2,3}$ level, because AgCl has a small ionic character and a strongly covalent character.

Conclusion

In this work, it has been shown that a spectral feature is closely connected with the chemical state and that the $L_{2,3}$ emission spectra are very useful for chemical-state analysis. The following properties have been found:

(1) The $L_{2,3}$ emission spectra of the highly ionic bond scarcely reveals any influence of the cations.

(2) The $L_{2,3}$ emission spectra for the molecular T_d symmetry of different central atoms have similar features.

(3) The peak related to the hydrogen atom is observed on the lower side of the middle peak in the $L_{2,3}$ emission spectra. This is suggests that the X-ray emission spectra give information about the existence of hydrogen in the chemical combination.

(4) In the $L_{2,3}$ emission spectra of the oxyanions, the middle peak shifts to the higher-energy side and its intensity decreases, while the peak of the higher-energy side increases according to the increase in the number of oxidation. It is reasonable to think that the oxygen 2p electron will diffuses into the 3d atomic orbital of the central atom in the valence molecular orbital when the central atom combines with oxygen.

(5) The spectral feature is influenced by the kind of ligand if this atom forms a part of the molecular orbital.

(6) In a highly ionic bond, the spectrum is simple, with two peak components. However, the spectrum is different according to its covalent character.

In this work, we can not interpret the spectra quantitatively as transitions from the molecular orbitals with the help of a molecular orbital calculation. This will remain a subject for future study.

The main program of this work was begun by the author during his stay at the University of Hawaii. The author wishes to express his thanks to Professor B.L.Henke for his kind guidance. We also gratefully acknowledge some very useful discussions with Dr. Sigero Ikeda of Osaka University and Dr. Yōichi Gōshi of Tokyo University, and the invaluable help of the undergraduate students in their laboratories.

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