Spectral Changes in X-Ray *K* Emission Lines of Potassium in Various Compounds

Seiji YASUDA* and Hitoo KAKIYAMA

The Government Industrial Research Institute, Kyushu, Shuku-machi, Tosu, Saga 841

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Synopsis. The chemical shifts and profile changes in the $K\alpha_{1,2}$, $K\beta_{1,3}$ and their satellite lines of potassium from 21 chemical compounds were measured with a two-crystal X-ray spectrometer. The data obtained are discussed qualitatively and related to the nature of the surrounding groups.

The valences or coordination numbers of elements in unknown samples or the ionic character of chemical bonds can be readily distinguished by the spectral changes in X-ray emission lines.[1] Such studies have received considerable attention from analytical chemists. However, so far as the elements such as potassium and calcium are concerned, only a few measurements have been directed to the theoretical interpretation of the $K\beta_{1,3}$ and its satellite lines.[2-4]

In the previous paper,[5] we have shown that the surrounding atoms or anions give appreciable line shifts and profile changes in the $K\alpha$ and $K\beta$ emission lines of calcium. The present note deals with potassium in an analogous way by measuring the chemical shifts and profile changes in the potassium $K\alpha_{1,2}$, $K\alpha_{3,4}$, $K\beta_{1,3}$, $K\beta''$, and $K\beta_5$ lines from 21 chemical compounds. The purpose for our previous and present studies is to examine whether a change of the nature of the surrounding groups leads to line shifts or profile changes in X-ray K emission lines of elements with constant formal charges in most compounds.

Experimental

The potassium X-ray emission spectrum was measured automatically by a step-scanning method at regular intervals of 0.005° 2θ using a Rigaku two-crystal X-ray spectrometer with Ge(111) crystals ($2d$=6.5327 Å). The primary radiation used for exciting the spectrum was provided by a chromium X-ray tube operated at 50 kV, 30 mA. The detector was a flow proportional counter. The 2θ position of the potassium $K\alpha_1$ was determined by averaging the goniometer settings at which the same intensity was measured on either side of the peak at the half-maximum intensity. The $K\alpha_2$, $K\alpha_4$, and $K\beta_{1,3}$ positions were also determined in the same way at approximately 70% intensity, whereas the $K\beta''$ and $K\beta_5$ positions were estimated from their apparent maxima. The chemical shift was calculated as an energy difference between the respective lines from the compound under study and KF. The experimental errors in such procedures were estimated to be±0.02 eV in the $K\alpha_1$, $K\alpha_2$, and $K\beta_{1,3}$ shifts and ±0.06 eV in the other lines. No corrections were made on the spectrum measured.

All potassium compounds used were of the highest commercial grade available and were confirmed by X-ray diffraction.

Results and Discussion

Potassium Kα *Spectrum.* The potassium $K\alpha$ emission spectrum consists of the $K\alpha_{1,2}$ doublet and its high energy satellites, namely the $K\alpha_{3,4}$ group. For all compounds, the $K\alpha_1$ full width at half-maximum intensity and the peak separation in the doublet seemed nearly constant at about 1.90 and 2.68 eV, respectively. In addition, the observed chemical shifts of both the $K\alpha_1$ and $K\alpha_2$ lines did not exceed the limits of the experimental errors at ±0.02 eV. The potassium $K\alpha_{3,4}$ group of satellites was observed on the high energy tails of the parent $K\alpha_{1,2}$ doublet. In every case, three components $K\alpha'$, $K\alpha_3$, and $K\alpha_4$ could be resolved, about 11, 18, and 22 eV apart from the $K\alpha_1$, respectively. However, there were no significant changes in the energy positions, profiles and relative intensities of the resolved satellite components in all compounds. These results indicate that the $K\alpha_{1,2}$ and its high energy satellite lines of potassium in different compounds are little affected by the changes of surrounding groups or of the crystal structures of compounds.

Potassium Kβ *Spectrum.* The potassium $K\beta$ spectrum from KF is shown in Fig. 1. According to the relative positions in similar spectra which have appeared in the literature,[2,6] the main peak was assigned to $K\beta_{1,3}$ and its high energy satellites were assigned to $K\beta''''$, $K\beta'''$, $K\beta_5$, and $K\beta''$ beginning from the high energy side in every case. The weak emission structures on the

Table 1. Characteristic data of the spectral changes in the potassium $K\beta$ lines

Compound	Chemical shift/eV			$\Delta E_{K\beta_{1,3}-K\beta_{1,4}}$
	$K\beta_{1,3}$	$K\beta''$	$K\beta_5$	eV
$K_2S_2O_8$	+0.10	0.0	−0.4	9.6
K_2SO_4	+0.05	0.0	−0.2	9.9
$KHSO_4$	+0.03	0.0	−0.2	9.9
KF	—	—	—	10.1
KH_2PO_4	+0.05	0.0	+0.1	10.2
$K_4P_2O_7$	+0.03	−0.2	+0.1	10.2
KNO_3	+0.03	−0.3	+0.6	10.7
K_2SO_3	+0.03	−0.2	+1.1	11.2
$KBrO_3$	+0.10	−0.2	+1.2	11.2
$KHCO_3$	+0.03	−0.3	+1.2	11.3
KNO_2	+0.03	−0.3	+1.2	11.3
$KClO_3$	+0.08	−0.3	+1.4	11.4
$KMnO_4$	+0.13	−0.3	+1.5	11.5
$KClO_4$	+0.10	−0.2	+1.5	11.5
$K_3C_6H_5O_7\cdot H_2O$	+0.05	−0.3	+1.7	11.8
$KOOCC_6H_4COOH$	+0.10	−0.3	+1.8	11.8
KCl	+0.05	−0.3	+1.8	11.9
K_2CO_3	+0.03	−0.3	+1.8	11.9
CH_3COOK	+0.05	−0.1	+2.1	12.2
KBr	+0.05	−0.4	+2.8	12.9
KI	+0.03	−0.4	+3.5	13.6

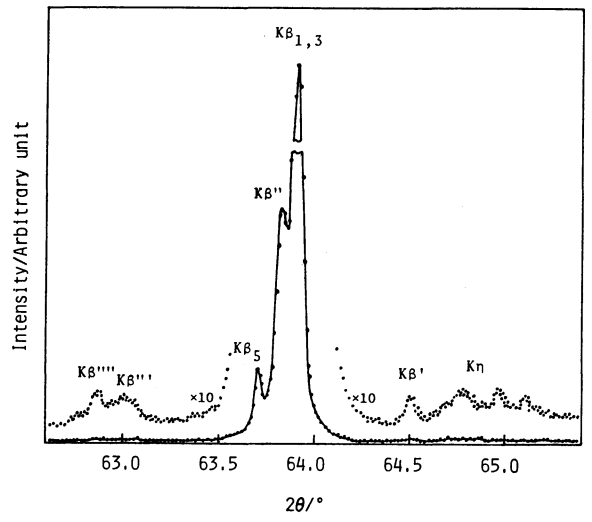

Fig. 1. Potassium $K\beta$ spectrum from KF.

low energy side of the $K\beta_{1,3}$ were assigned to $K\beta'$ and $K\eta$. The observed spectrum of each compound was characterized by the chemical shifts of the $K\beta_{1,3}$, $K\beta''$, and $K\beta_5$ relative to the respective lines in KF and the energy difference (ΔE) between $K\beta_5$ and $K\beta_{1,3}$. The measured data of these four parameters are listed in Table 1, according to the increase of the last parameter.

The potassium $K\beta_{1,3}$ line had an almost constant full width at half-maximum intensity of 1.67 eV for all compounds, but a slight difference in the energy positions was detectable. The experimentally observed shifts of the $K\beta_{1,3}$ lay in the range +0.03 to +0.13 eV, although they rarely exceeded +0.05 eV. However, a simple correlation in relating the observed $K\beta_{1,3}$ shifts to the nature of surrounding atoms or anions could not be found. The potassium $K\beta''$ bands was found to occur at about 4 eV higher energies than those of the $K\beta_{1,3}$. This band of most compounds was shifted slightly to lower energies by 0.1—0.4 eV relative to that of KF. The $K\beta''$ is generally regarded as a satellite, but the origins of this band and the observed shifts are at present unclear.

At 10—14 eV above $K\beta_{1,3}$, the potassium $K\beta_5$ band appeared as a well-defined peak in the spectra from potassium halides, carbonate and nitrate, while the other compounds gave the broad asymmetric $K\beta_5$ band with some structure and an ambiguous maximum. The chemical shifts of this band were as much as several electron Volts in the range −0.4 to +3.5 eV; these shifts are remarkably larger than those of the $K\beta_{1,3}$ and result in an increase in the energy difference ΔE with increasing the $K\beta_5$ shifts toward higher energies; these are shown in the last two columns of Table 1. A similar trend has been found by the photographic determinations of the potassium $K\beta_{1,3}$ and $K\beta_5$ energies from potassium carbonate, sulfate, and halides.[6] Since the $K\beta_5$ bands of potassium sulfates and phosphates shifted slightly to lower energies by 0.2—0.4 eV and to higher energies by 0.1 eV, respectively, the energy difference ΔE in these compounds was rather close to the value 10.1 eV for the reference material, KF. The remaining compounds showed the $K\beta_5$ shifts in the range +0.7 to +3.5 eV, which are almost comparable to those of calcium compounds.[5] On the other hand, the energy differences ΔE by 11—12 eV in most compounds were about 0.5 times as large as those in calcium compounds. In a series of potassium halides, the $K\beta_5$ maximum was found to shift toward higher energies with a decrease in the electronegativity of surrounding atoms with a consequent decrease in the charge of the potassium atom. This finding was the only possible regularity obtained in the present study on the spectral changes in the potassium X-ray K emission lines.

Every measured spectrum revealed very broad high energy structures $K\beta''''$ and $K\beta'''$ at about 53 and 44 eV above $K\beta_{1,3}$ and the low energy structures $K\beta'$ at about 31 eV below $K\beta_{1,3}$ and $K\eta$ with several maxima mostly occurring at about 42, 52, and 60 eV below $K\beta_{1,3}$. However, their profile changes and line shifts could not be investigated in detail because of the extremely faint intensities.

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