The X-Ray Emission Spectra of the Compounds of Third-period Elements. I. The *K* Spectra of Chlorine in Compounds

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On chlorine gas and several oxysalts of chlorine, the values of the wavelength shift of Cl$K\alpha_{1,2}$ lines and the spectra of Cl$K\beta$ lines were measured. We thus verified our assumption that the $K\beta'$ line results from the bias of valence electrons from the atom of the third-period element to the oxygen atom in the oxyanion; this can be explained in terms of the relationship between the chemical structure and the Cl$K\beta$ spectrum of the hypochlorite ion. The relationship between the relative intensity of the $K\beta'$ line and the wavelength shift of the $K\alpha_{1,2}$ lines was linear, just as in the cases of oxygen-sulfur compounds.

In previous papers, we reported our studies of the wavelength shifts of S$K\alpha_{1,2}$ lines and the shapes of the S$K\beta$ band spectra in many sulfur compounds.[1-3] It was found that a linear relation exists between the relative intensity of the S$K\beta'$ satellite line and the wavelength shift of the S$K\alpha_{1,2}$ lines in the spectra of oxygen-sulfur compounds. We think that this relationship offers a key for the assignment of the $K\beta'$ satellite line, which we have not yet been able to decide clearly. Therefore, in order to ascertain the generality of this relationship, we intend to extend our investigation to other elements of the third-period. In this paper, we will report on the $K\beta$ spectra of several chlorine compounds, particularly on the character of the $K\beta'$ line.

Recently, Best investigated the Cl$K\beta$ spectra of some oxysalts of chlorine.[4] Schnell measured the Cl$K\beta$ spectra on several chlorine compounds.[5] LaVilla and Deslattes measured the $K\beta$ spectra on some gaseous chlorine compounds.[6] On hypochlorite and chlorine gas, though, the K spectra have not yet been examined.

Experimental

The apparatus was the same as that described in previous papers.[1,3] A Machlett Wolfram target X-ray tube OEG-50 was operated at 40 kV, 40 mA. A flat, germanium analyzing crystal (2d: 6.53272 Å) was used. The helium path was maintained using a flow of 1.5 *l*/min at ordinary pressure. For the measurement of the spectrum of chlorine gas, a gas-sample cell was used.[7]

The wavelengths of the $K\alpha_{1,2}$ lines were measured as follows: the X-ray intensities were counted for a minute at intervals of $1'(2\theta)$; then, after drawing the spectral curve, the position of the line was decided as the maximum intensity position (the average of triplicates). In actual measurement, the wavelength shifts from the Cl$K\alpha_{1,2}$ lines of sodium chloride were measured. The absolute wavelength value of the Cl$K\alpha_{1,2}$ lines of sodium chloride was decided by comparison with the third-order line (4.62150 Å) for Cu$K\alpha_1$. The spectrum of the $K\beta$ lines was obtained as follows: the X-ray intensities were measured of a minute at intervals of $3'(2\theta)$, and then, after the substraction of the background (X-ray intensity at 4.54 Å), these intensities were plotted against the wavelength. Each spectrum was made on the same scale at the maximum intensity.

The separation of the $K\beta$ spectrum into several peaks was done as follows: 1) assuming that the $K\beta$ spectrum of sodium chloride can be taken as the standard shape of the C peak in Fig. 1, 2) to separate the C peak from each spectrum, this curve was superposed on the highest peak of each spectrum; 3) the A and D peaks were separated by the subtraction of C peak from the original spectrum. By the way, Best had reported in his paper the presence of a $K\beta_x$ satellite line at the short-wavelength side of the $K\beta_1$ line in the spectrum of sodium chloride,[4] but we could not separate them. Therefore, the present method might have a chance of mistakes in the separation of the D peak from the spectrum, but for the A peak ($K\beta'$ line) there can be no mistake.

A solution sample of sodium hypochlorite was prepared as follows: 1) to eliminate impurities (mainly chloride), a mixture of some higher bleaching powder and a small amount of cooled water was slowly stirred for ten or more minutes, and subsequently filtered. 2) The precipitate was dispersed into water and then, after about 30 min, filtered. 3) The filtrate was converted into a solution of sodium salt. The sample prepared by this method contained 0.80M hypochlorite and 0.09N chloride (impurity). After X-ray irradiation for two hours, the sample lost 5 percent of the hypochlorite and the equivalent amount of chloride was increased.

Results

In Fig. 1a—f, we show the Cl$K\beta$ spectra of the element and five compounds. The shapes of the spectra are similar to those of sulfur compounds which show a corresponding chemical structure, *i. e.*, chloride to inorganic sulfide, chlorate to sulfite, and perchlorate to sulfate, respectively. The characteristic values of the Cl$K\alpha_{1,2}$ lines and Cl$K\beta$ lines of the element and five compounds are listed in Table 1. In order to compare these data with the data of sulfur compounds, the directly-measured values of the energy shift in the $K\alpha_{1,2}$ lines of sodium chloride were converted to those of the element (Cl_2 gas). The intensity ratio of the $K\beta'$ line is defined as the ratio of the area of the $K\beta'$ line (the A peak in Fig. 1) to the total area of the $K\beta$ lines in the spectrum. A linear relationship exists between the

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[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] P. E. Best, *J. Chem. Phys.*, **49**, 2797 (1968).

[5] E. Schnell, *Monatsh. Chem.*, **93**, 1383 (1962).

[6] R. E. LaVilla and R. D. Deslattes, *J. Chem. Phys.*, **45**, 3446 (1966).

[7] The details of the gas-sample cell will be given by T. Sato *et al.*, in another paper.

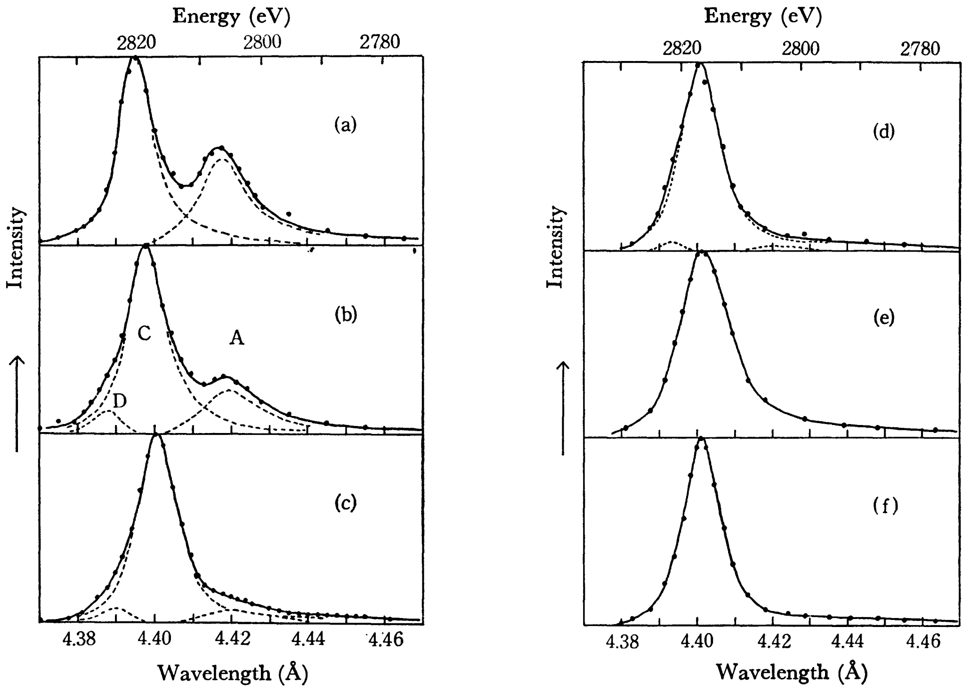

Fig. 1. a—f. *Kβ* spectra of chlorine in compounds.
a: sodium perchlorate, b: sodium chlorate, c: sodium chlorite, d: sodium hypochlorite, e: chlorine gas, f: sodium chloride. A: *Kβ'* line, C: $K\beta_1$ line.

TABLE 1. THE CHARACTERISTIC VALUES ABOUT THE Cl$K\alpha_{1,2}$ AND Cl$K\beta$ LINES

	$K\alpha_{1,2}$		$K\beta$			
				Intensity Ratio		
	λ (Å)	ΔE(eV)	λ(Å) C	A	C	D
NaCl	4.72949	−0.22	4.4015	0.00	1.00	0.00
Cl_2	909	±0.00	4.4005			
NaOCl	909	±0.00	4.4005	0.01	0.98	0.01
$NaClO_2$	872	+0.22	4.4000	0.09	0.86	0.05
$NaClO_3$	753	+0.87	4.3983	0.23	0.71	0.06
$NaClO_4$	660	+1.38	4.3955	0.37	0.63	0.00
Error		±0.07		±0.02		±0.02

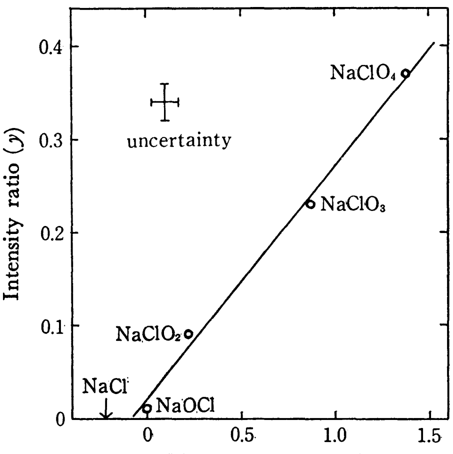

Fig. 2. Relationship between the intensity ratio and the energy shift of $K\alpha_{1,2}$ lines about chlorine compounds.
$y = 0.25x + 0.02$

intensity ratio of the *Kβ'* line and the energy shift of the $K\alpha_{1,2}$ lines,[8] as is shown in Fig. 2.

Discussion

On the intensity ratio of the Cl*Kβ'* line of the perchlorate, our value (sodium salt) is 0.37, but Best's (potassium salt) is 0.225,[4] in terms of the present definition. Under X-ray irradiation, potassium per-

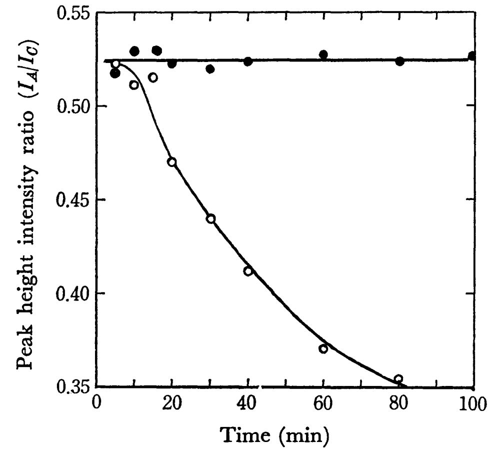

Fig. 3. Variation of the intensity ratio ($K\beta'/K\beta_1$) about perchlorates.
● $NaClO_4$ ○ $KClO_4$

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[8] The energy shift of the $K\alpha_{1,2}$ lines relates to the effective charges of the chlorine atom in a compound.[9-11]

[9] E. Clementi, *Table of Atomic Functions, Suppl. to IBM J. Research and Development*, No. 1 (1965).

[10] W. S. Urusof, *Dokl. Akad. Nauk SSSR*, **166**, 660 (1966).

[11] W. I. Nefedow, *Phys. Status Solidi*, **2**, 904 (1962).

chlorate was decomposed to chloride,[12] and so its $K\beta'$ ratio was rapidly lowered, as is shown in Fig. 3. Moreover, his sample was placed in a vacuum; this might have caused the more rapid decomposition in his measurements. We adopted only the value of sodium salt.

In the previous paper,[3] we reported that the relative intensity of the $K\beta'$ line increased as the number of the valence electrons of the sulfur atom decreased. Therefore, we now presume that the $K\beta'$ line occurs as a result of the bias of valence electrons from the atom of the third-period element to the oxygen atom in the oxyanion. In the Cl$K\beta$ spectrum of a hypochlorite solution, the $K\beta'$ line is little observed; nevertheless, the oxygen atom is present in its molecule (see Fig. 1d). This result is explainable on the basis of the chemical structure of the hypochlorite ion (Cl–O$^-$) and our presumption relating to the occurrence of the $K\beta'$ line. That is, in this oxyanion, 1) the chlorine atom is combined with a oxygen atom by a single bond. The electron-inductive effect of the oxygen atom in a single bond is less than that of the oxygen atom in a double bond, and 2) the difference in the electronegativity between the oxygen atom (3.5) and the chlorine atom (3.0) is small. Moreover, the force of the electron attraction of the oxygen atom becomes weakened as a result of the acceptance of electrons from the sodium atom to the oxygen atom. Therefore, the valence electrons of the chlorine atom will be little attracted by the oxygen atom (indeed, the energy shift of Cl$K\alpha_{1,2}$ lines of this sample was small, if present at all). Consequently, from the above presumption, it may be concluded that the $K\beta'$ line occurs to only a small extent in the spectrum of hypochlorite. The above explanation serves to verify the assumption relating to the occurrence of the $K\beta'$ line.

For further discussion, we show the relationship between the relative intensity of the $K\beta'$ line and the energy shift of the $K\alpha_{1,2}$ lines for chlorine compounds in Fig. 2, and that for sulfur compounds,[3] in Fig. 4. To our surprise, the two relationships are expressed by the same straight line. From the fact that the straight line runs near the point of origin, there might be no other dominant factor which contributes to the occurrence of the $K\beta'$ line other than the energy shift of the $K\alpha_{1,2}$ lines, namely, the effective charges of the atom. From the equality of the gradient of the two lines, we cannot but think that the gradient of the line is determined by neither the sulfur atom nor the chlorine atom, but only by the oxygen atom, in oxygen-compounds. Nefedow claimed in his paper that, on the compound of the third-period element having second-period elements, the $K\beta'$ line was related to the electron transition from the molecular orbital to the 1*s* state of the third-period element, that this molecular orbital could virtually be regarded as the 2*s* orbital of the second-period element.[13] Our results seem to be consistent with his deduction.

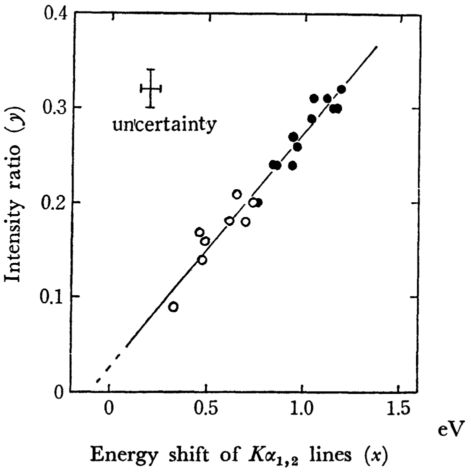

Fig. 4. Relationship between the intensity ratio and the energy shift of $K\alpha_{1,2}$ lines about sulfur compounds.
●: sulfate or sulfone ○: sulfite or sulfoxide
$y = 0.25x + 0.02$

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[12] We detected the presence of a little chloride in the X-ray irradiated sample which had discolored to a yellow-brown upon titration with silver nitrate.

[13] W. I. Nefedow, *Zh. Struk. Khim.*, **8**, 686, 1037 (1967).