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

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On sixteen compounds of phosphorus, the wavelength shifts of the $K\alpha_{1,2}$ lines and the fine structures of the $K\beta$ band of the phosphorus emission spectra were measured. For the oxygen compounds, the relationship between the intensity ratio of the $K\beta'$ line and the energy shift of the $K\alpha_{1,2}$ lines was found to be expressed by a straight line similar to that found for sulfur and chlorine compounds. In the spectra of the oxyacids and their salts, the intensity ratio of the satellite line which is observed between the $K\beta_1$ and $K\beta'$ lines is proportional to the number of the hydroxyl groups in a molecule. The appearance of this line seems to be attributable to the covalent bond between a third-period atom and a non-ionized atom. In the $K\beta$ spectrum of triphenyl phosphite, the strong satellite line at the highest energy site seems to have a nature similar to those found in sulfite, chlorate, and phosphorus trichloride.

Previously, we have studied the nature of the satellite line $K\beta'$ which is observed on the longer-wavelength side of the $K\beta_1$ line of sulfur and chlorine in many kinds of oxygen compounds, and have found that the relationship between the ratio of the integral intensity of the $K\beta'$ line to the total intensity of the $K\beta$ line (we call it the intensity ratio of the $K\beta'$ line) and the energy shift of $K\alpha_{1,2}$ lines (it relates to the effective charges of the atom in a molecule[1,2]) can be expressed by straight line similar to those for the oxygen compounds of both sulfur and chlorine. From these facts, it has been suggested that the appearance of the $K\beta'$ line is due to the transfer of valence electrons from the third-period atom to the bonded oxygen atoms in the molecule, and that its intensity is related to the nature of the ligand atoms rather than to the kind of third-period atom.[3,4]

In order to check the general truth of these facts as regards all the third-period elements, the P$K\beta$ spectra of various phosphorus compounds have been measured. Although the data on the P$K\alpha_{1,2}$ lines have been already reported by Yao and Holst,[5] and more recently by Nikolaev *et al.*,[6] new measurements are now made for several compounds.

Experimental

The spectra were measured on the same apparatus as that descrived in a previous work.[4] A flat germanium analyzing crystal ((111) plane, 2*d*: 6.53272 Å) was also used. The wavelength values of the P$K\alpha_{1,2}$ lines on each compound were measured, using the fourth-order reflection of the Cu$K\alpha_1$ line (corresponding to 6.16200 Å) as the standard; they were then converted to the value of the energy shift from the value of red phosphorus. The spectra of P$K\beta$ were obtained using the step-by-step method as in the previous work. However, in the case of phosphorus trichloride, in order to avoid the oxydation of the material during the measurements, the spectrum was obtained by the chart-recording method (one running time was 12 min), and the average of the three runs was taken. The background was measured at the 5.90 Å position. The separation of the $K\beta$ spectrum into several component peaks was attempted, taking the P$K\beta_1$ peak of anhydrous sodium phosphate as the standard shape.

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[1] C. A. Coulson and C. Zauli, *Mol. Phys.*, **6**, 525 (1963).

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

[3] Y. Takahashi and K. Yabe, This Bulletin, **42**, 3064 (1969),

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

[5] T. C. Yao and J. J. Holst, *Spectrochim. Acta*, **23B**, 19 (1967).

[6] A. V. Nikolaev, L. N. Mazalov, A. P. Sadovskii, V. V. Murachtanov, E. A. Gal'tsova, T. I. Gujavina, and N. I. Yakovleva, *Dokl. Akad. Nauk SSSR*, **189**, 784 (1969).

Results and Discussion

The P$K\beta$ spectra measured are shown in Fig. 1. We named the component peaks as is shown in Fig. 1, *i.e.*, A($K\beta'$), B, C($K\beta_1$), C′, and D, counting from the longer-wavelength side. The structure of the spectrum of red phosphorus was so complicated that the separation into component peaks was not attempted for this substance. The characteristic values of the $K\alpha_{1,2}$ and $K\beta$ lines for each compound are summarized in Table 1.

Table 1. Characteristic values of the $K\alpha_{1,2}$ and $K\beta$ lines measured for various compounds of phosphorus

	$K\alpha_{1,2}$		$K\beta$, λ(Å)			Intensity ratio (%)				
	λ(Å)	ΔE(eV)	A	C	D	A	B	C	C′	D
P_4(red)	6.15837			5.7940						
Na_3PO_4	5595	0.79	5.8370	5.7990		0.26		0.74		
Na_2HPO_4	5605	0.76	8365	7985		0.26	0.08	0.66		
NaH_2PO_4	5592	0.80	8380	7985		0.25	0.14	0.57	0.04	
H_3PO_4	5595	0.79	8380	7990		0.24	0.27	0.34	0.15	
$Na_4P_2O_7$	5595	0.79	8365	7980		0.28	0.08	0.62	0.02	
$(NaPO_3)_3$	5585	0.82	8375	7990		0.24	0.17	0.38	0.21	
$(P_2O_5)_2$	5585	0.82	8380	8050		0.21	0.13	0.33	0.33	
$(\phi O)_3PO$	5624	0.70	8400	8095	5.781	0.18	0.13	0.34	0.30	0.05
PCl_5	5655	0.59	8195	7955	781	0.25	0.10	0.61		0.04
Na_2HPO_3	5637	0.66	8375	7995		0.22	0.06	0.68	0.04	
H_3PO_3	5650	0.59	8395	8010		0.20	0.14	0.49	0.17	
$(\phi O)_3P$	5672	0.54	8430	8090	786	0.10	0.10	0.21	0.30	0.29
PCl_3	5710	0.41	8205	7970	785	0.16	0.04	0.61		0.19
NaH_2PO_2	5690	0.48	8930	8000		0.18	0.08	0.68	0.06	
H_3PO_2	5701	0.45	8400	8005		0.11	0.16	0.57	0.13	
							B′ 0.03			
Error (2σ)		±0.07	±0.0010	±0.0010		±0.02	±0.03	±0.03	±0.03	±0.03

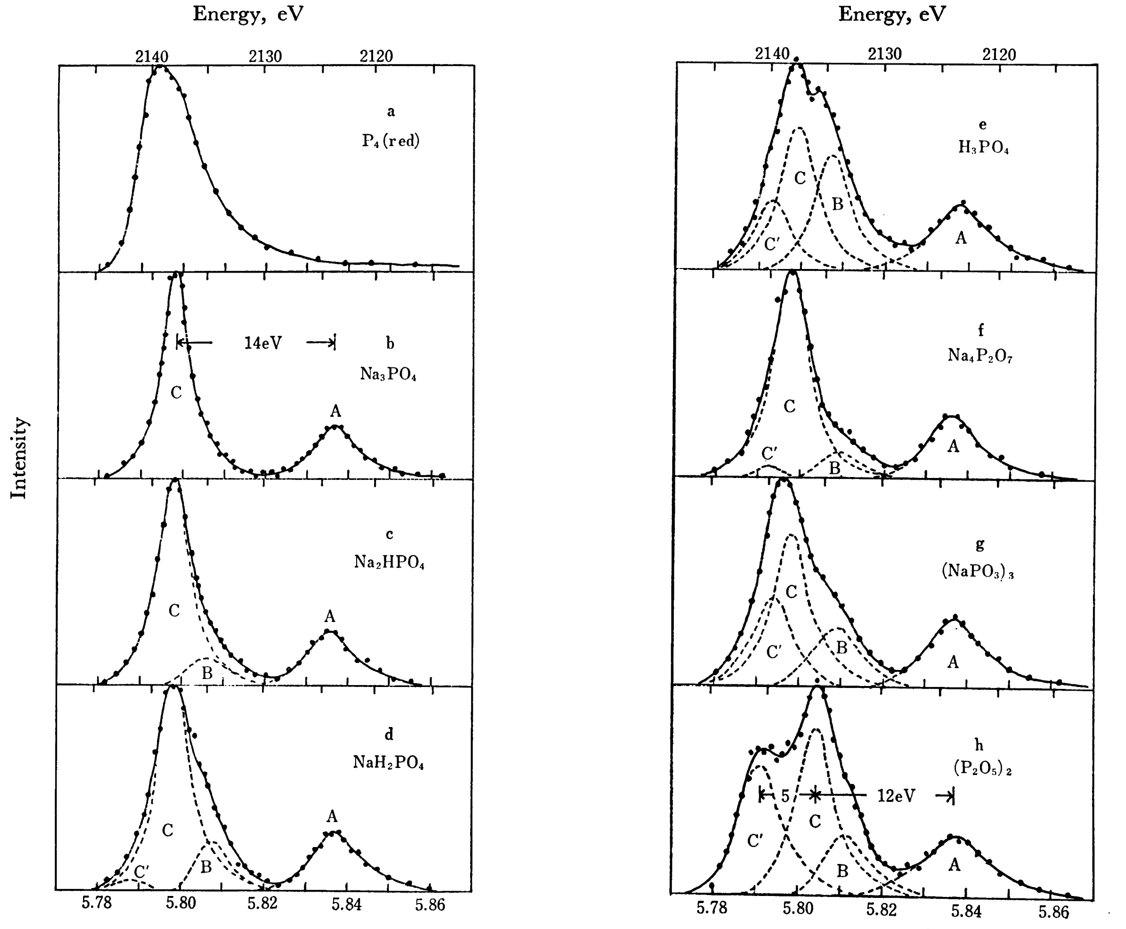

Fig. 1-A. P$K\beta$ spectra.

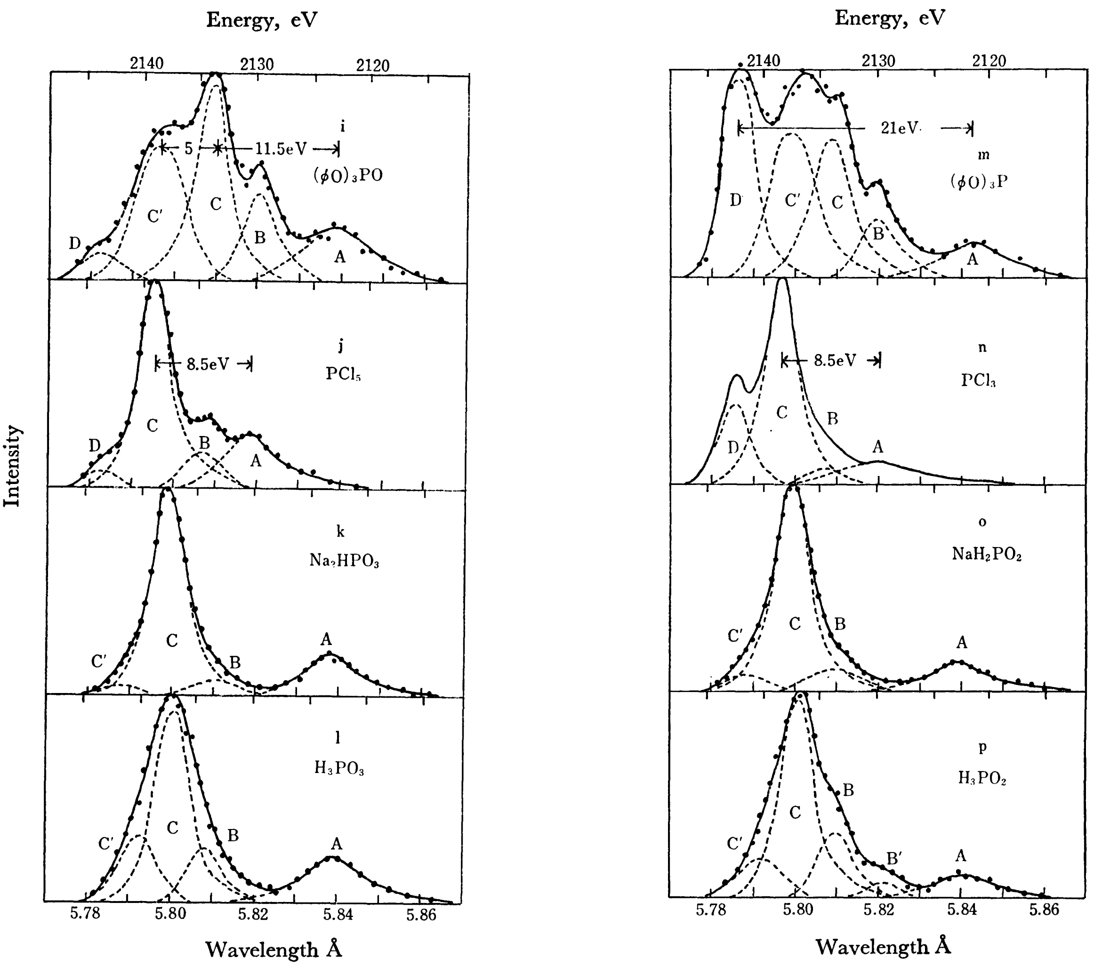

Fig. 1-B. P*K*β spectra.

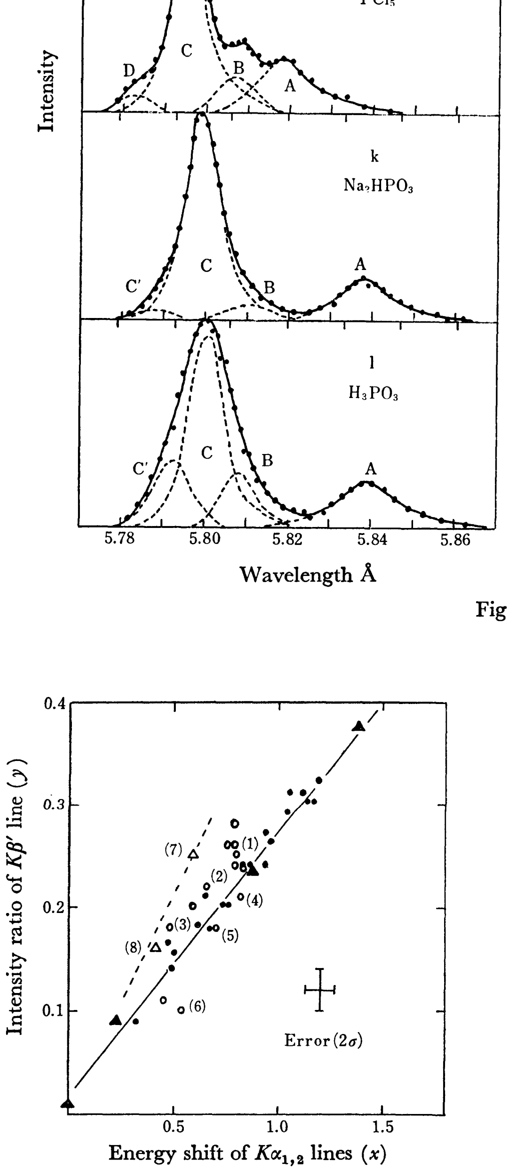

Fig. 2. The relationship between the intensity ration of $K\beta'$ line and the energy shift of $K\alpha_{1,2}$ lines.

○: oxygen-compound of phosphorus (P*K*β), (1) Na_3PO_4, (2) Na_2HPO_3, (3) NaH_2PO_2, (4) $(P_2O_5)_2$, (5) $(\phi O)_3PO$, (6) $(\phi O)_3P$.

△: chloride of phosphorus (P*K*β), (7) PCl_5, (8) PCl_3.

●: oxygen-compound of sulfur (S*K*β)

▲: oxygen-compound of chlorine (Cl*K*β)

——: regression line relating to the oxygen-compounds of sulfur and chlorine, $y=0.25\,x+0.02$.

------: anticipated line relating to the compounds of chlorine ligand.

The relationship between the $K\beta'$ intensity ratio and the energy shift of the $K\alpha_{1,2}$ lines found in the oxygen compounds and chlorides of phosphorus (mark ○ and △, respectively) is shown in Fig. 2. Although the points for the oxygen compounds are scattered in some extent, it may be concluded that they lie on a straight line similar to that found in the oxygen compounds of sulfur and chlorine. To speak more exactly, the points for the oxysalts of phosphorus drop on the upper side of the line, while those for the molecular oxygen compounds (phosphorus pentoxide P_2O_5, triphenyl phosphate $(\phi O)_3PO$, *etc.*) lie on the lower side. The points for phosphorus pentachloride and phosphorus trichloride deviate much from the line (mark △). It might be presumed that the latter points lie on another line, having a larger gradient. From this fact, it seems that the gradient of the line in the Fig. 2 is related not to the kind of third-period atom in the molecule, but to the kind of ligand atom.

In the $K\beta$ spectra of the oxygen compounds of sulfur and chlorine, and in those of the oxysalts of phosphorus, the energy difference between A and C was measured to be about 14 eV. However, in the case of the molecular oxygen compounds of phosphorus (P_2O_5, $(\phi O)_3$-PO, *etc.*), the energy difference between A and C is about 12 eV, and there is a strong C' peak separated about 5 eV from the C peak on the higher-energy side. On the other hand, in the $K\beta$ spectra of the chlorides

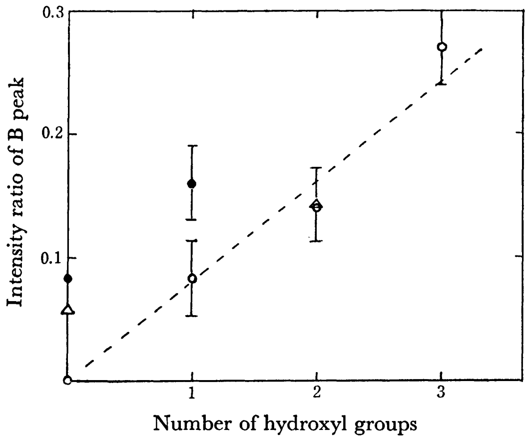

Fig. 3. The relationship between the intensity ratio of B peak and the number of hydroxyl groups in the oxyacids and their salts.

○: phosphoric acid (sodium salt)
△: phosphorous acid (sodium salt)
●: hypophosphorous acid (sodium salt)

We supposed that hypophosphorous acid was monobasic, in this Figure. We did not adupt the B′ peak, but adupted only the B peak on the intensity ratio of hypophosphorous acid.

of phosphorus, the energy differece between A and C was about 8.5 eV. The difference in these two cases may be compared with the difference in the gradients of the two lines in Fig. 2.

As in the case of the sulfur compounds, in which the B peak is observed in the *Kβ* spectrum of such molecular compounds as dimethyl sulfone and the *N,N*-derivative of sulfoneamide,³⁾ the B peak is also observed in the molecular compounds of phosphorus, such as phosphorus pentoxide, triphenyl phosphate, and phosphorus pentachloride. In addition, in the oxysalts and oxyacids of phosphorus, the intensity of the B peak is proportional to the number of hydroxyl groups in the molecule.⁷⁾ In the spectrum of anhydrous sodium phosphate, which does not have a hydroxyl group, the B peak is, as expected, not observed. This relationship is shown in Fig. 3. Considering the position of the points for phosphite and hypophosphite in the figure, it seems that the P–H bond of these compounds slightly affects the appearance of the B peak. The appearance of the B peak seems to be attributable to the covalent bond between a third-period atom and a non-ionized atom, such as P–OH, P–OC, and P–OP. On sodium pyrophosphate, $[^-O_3P{-}O{-}PO_3{}^=]\cdot 4Na^+$, which involves only one such covalent bond per phosphorus atom, the B peak intensity ratio is close to the value in disodium hydrogenphosphate, and while on sodium metaphosphate, $^-O_2P\langle^{O-PO_2^-}_{O-PO_2^-}\rangle O\cdot 3Na^+$, which has two such covalent bonds per phosphorus atom, the ratio is close to the value in sodium dihydrogenphosphate. Further, on phosphorus pentoxide (dimer), in which there are one and a half such covalent bonds per phosphorus atom, the value of the ratio is conformable to the number of the covalent bond (see Table 1).

The D peak, as has been mentioned in a previous work, was markedly observed in the S*Kβ* spectra of sulfite and sulfoxides and in the Cl*Kβ* spectrum of chlorate.³,⁴⁾ As for the phosphorus compounds, a remarkable D peak is also observed in the spectrum of phosphorus trichloride. Generally, it seems that the remarkable D peak is observed in the *Kβ* spectrum of the compound in which the third-period atom has one lone pair, such as $SO_3{}^=$, $ClO_3{}^-$, SF_4,⁹⁾ and PCl_3. The phosphorus atom of triphenyl phosphite $(\phi O)_3P$ also has one lone pair, so the appearance of the remarkable D peak in the spectrum can be anticipated. The D peak in the *Kβ* spectrum measured (Fig. 1m) seems to correspond to the D peak of the sulfite or the phosphorus trichloride in view of the position and the intensity of the peak. That is, the peak appears in nearly the same position as the D peak of the phosphorus trichloride, and the peak separation between A and D in the spectrum of Fig. 1m, about 21 eV, corresponds to that between A and D for the sulfite, 21 eV, and to that for the chlorate, 20 eV. The intensity ratios of the D peak to the total *Kβ* line in these compounds (0.29, 0.19, and 0.14 for triphenyl phosphite, phosphorus trichloride, and sodium sulfite, respectively) are larger than in other compounds.

The C′ peak is observed in the spectra of phosphorus pentoxide, triphenyl phosphate, and triphenyl phosphite. This peak can be distinguished from the D peak as a result of the difference in the position of the C′ peak (5.790—5.800 Å) from that of the D peak (5.783—5.787 Å). For example, in the spectrum of triphenyl phosphite, both D and C′ peaks are observed, and they can be distinguished, as is shown in Fig. 1m.

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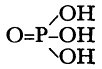
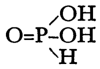
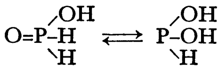
7) To make the matter clearer, the chemical structures of these oxyacides are shown below:


$\mathrm{O{=}P(OH)(OH)(OH)}$


$\mathrm{O{=}P(OH)(OH)H}$


$\mathrm{O{=}P(OH)(H)H \rightleftarrows P(OH)(OH)H}$

phosphoric acid, (tribasic)   phosphorous acid, (dibasic)   hypophosphorous acid, (monobasic)

in which dibasic inorganic hypophosphites are not present.⁸⁾

8) "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, (1962), p. 873.

9) In the S*Kβ* spectrum of sulfur tetrafluoride, the intensity ratio of the D peak is 0.13, the peak separation between the D and C peaks is 7.2 eV, and that between the C and A peaks is 18.5 eV.¹⁰⁾

10) Y. Takahashi, (unpublished data).