$K\alpha$ x-ray satellites of P, S, Cl, K, and Ca excited by photons

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 $K \alpha \underline{L}^1$ x-ray satellite spectra of P, S, Cl, K, and Ca excited by Rh x rays are studied employing a plane crystal spectrometer. Aberg's theoretical $I(K\underline{L}^1)/I(K\underline{L}^0)$ intensity ratios based on a free Ne core are found to be overestimations for Z > 15. The average $K\underline{L}^1$ satellite group energy shifts from that of $K\underline{L}^0$ of P, S, and Cl are found to be in general agreement with Dirac-Fock evaluations of Maurer *et al.* up to 3 to 4 *M* electrons.

I. INTRODUCTION

Single K plus multiple L-shell ionization gives rise to K_{α} x-ray satellites. These are designated as $K\underline{L}^{N}$ where N is the number of L holes. If N = 0, it denotes the normal K_{α} x ray, also called diagram line $(K\underline{L}^{0})$. In recent years, these satellites have been studied by heavy-ion excitation.^{1,2} However, the first one or two satellites can also be studied by electron or photon excitation.³⁻⁸ Though such studies are available, no systematic investigations seem to have been made for Z > 14, particularly by photon excitation. Recently, studies have been carried out by the authors⁸ by photon excitation in Cl. In the present investigations, results have been reported on $K_{\alpha} \underline{L}^{1}$ satellites of P, S, K, and Ca studied by photon excitation including that⁸ in Cl.

II. EXPERIMENT

The principle and the method of experimental procedures on the studies of K_{α} x-ray satellites by photon excitation are already reported.^{4,8} In the present investigations a Philips 1410 wavelength dispersive spectrometer is used. This, in brief, consists of a Rh x-ray tube, a plane

crystal spectrometer, and a continuous gas flow counter. 5-mm-thick and 50-mm-diameter pellets made out of powders of the compounds of P, S, K, and Ca are used. Two fine collimators (0.01°), one at the target and the other at the gas flow counter are used. The spectra are taken in 2θ steps of 0.02° to 0.05°. Details of the crystals and materials used are given in Table I. The energy calibration for Ge(111) and LiF(200) plane crystals is carried out using the reported^{9,10} $K_{\alpha} \underline{L}^{0}$ energies of P, S, and Cl and K, Ca, and Co $(K\alpha_2)$, respectively. Typical $K\alpha \underline{L}^1$ satellite spectra of P, S, K, and Ca are shown in Figs. 1 and 2. The spectra are analyzed and the average $K\alpha$ xray energies and their relative intensities are estimated. In the case of P the average satellite group energy is estimated by taking the weighted average energy of the multiplets $K\alpha_1$, $K\alpha_3$, and $K\alpha_4$ in their respective relative intensity proportions. Since in all the cases compounds are used, the effect of chemical energy shifts may be there even though small. However, the reported $K \alpha \underline{L}^0$ energies of pure elements are employed for the energy calibration. Hence, this effect would be mostly compensated. In any case, the reproducibility of the $K\alpha L^0$ energies used from the calibration fits are well within the errors reported in the $K \alpha L^0$ energies. The relative intensities are corrected for (i) crystal reflectivity, (ii) self-absorption in the foil, (iii)

TABLE I. Compounds of the elements, crystals, and other details.

Z	Element	Compound	Crystal	2 <i>d</i> Å	Order studied
15	Р	Na_2PO_3	Ge(111)	6.532	I
16	S	Na_2SO_3	Ge(111)	6.532	Ι
17 ^a	Cl	KCl	Ge(111)	6.532	Ι
19	K	KCl	LiF(200)	4.0767	Ι
20	Ca	CaCO ₃	LiF(200)	4.0767	Ι
26 ^a	Co	CoCO ₃	LiF(200)	4.0767	II

^aUsed for energy calibration along with others.

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FIG. 1. $K\alpha$ x-ray spectra of P and S.



FIG. 2. $K\alpha$ x-ray spectra of K and Ca.

	Photon excitation	Electron excitation		Theory
Element	Present work	Fischer et al. ^a	Parrat ^b	Aberg
Р	6.4±0.6	6.2±0.4 (P)		6.8
S	4.6±0.4	5.6±0.4 (S)	4.8 (S)	5.7
\mathbf{Cl}^{d}	3.4±0.4			4.8
K	$2.8 {\pm} 0.3$		2.6 (K_3PO_4)	3.5
Ca	$2.2{\pm}0.2$		2.2 (CaO)	3.1

TABLE II. $K\underline{L}^{1}/K\underline{L}^{0}$ intensity ratio (in %).

^aReference 7.

^bReference 6.

^cReference 3.

^dData of Cl of KCl reported earlier by the authors (Ref. 8). The elements or compounds used by the other authors are given in the parentheses of their respective values.

absorption in the counter window, and (iv) efficiency of the detector. However, this effect is rather negligibly small as the energy difference between $K\alpha \underline{L}^0$ and $K\alpha \underline{L}^1$ is small. But the estimated relative intensities may be uncertain by 10% or so because of the chemical effects, as compounds of the elements are used. This effect in the oxides of the low-Z elements like Mg, Al, and Si are found to be of the order of 10 to 12%. However, the errors in the present ratios are of the order of 10%.

III. RESULTS AND DISCUSSION

The estimated $I(K\underline{L}^1)I(K\underline{L}^0)$ intensity ratios are presented in Table II along with the available electron excitation and theoretical data of Aberg³ estimated on the assumption of Ne-like atoms. It can be seen from the table that there seems to be general agreement with the available experimental data by electron excitation within the range of experimental errors. However, even after considering the chemical effects, the theoretical data of Aberg³ are found to be overestimated for Z > 15. In Table III the present $K\alpha$ x-ray energies are compared with the available heavy-ion excitation data.^{1,11,12} In these cases also there seem to be general agreement among all the data within the range of errors. In Table IV the present $K\underline{L}^1$ satellite energy shifts from that of $K\alpha \underline{L}^0$ are compared with the available heavy-ion excitation data as well as with the theoretical data based on Dirac-Fock evaluations with variable number of M electrons, recently reported by Maurer et al.¹³ Maurer et al.¹³ presented 2p- 1s transition energies based on average of configurations of total energies in their theoretical evaluations for the estimation of $K\alpha$ x-ray shifts caused by the presence of M electrons. Since the difference of the two energies reported for $K\alpha \underline{L}^1$ satellite multiplets is small, only the simple averages are used for the estimation of the average $K\alpha \underline{L}^1$ satellite group energy shifts from that of $K\alpha \underline{L}^0$. It can be seen from the table that there is

TABLE III. $K\alpha$ x-ray energies in electron volts.					
Element		Present work Photon excitation	Demarest <i>et al.</i> ^a Heavy-ion excitation	Watson <i>et al.</i> ^b Heavy-ion excitation	Olsen <i>et al.</i> ^c Heavy-ion excitation
Р	<u>К</u> <i>L</i> ⁰	2013.6±0.4	2013.4±0.3		
	$K\underline{L}^{1}$	2026.4±0.6	$2026.0 {\pm} 0.3$		
S	<u>К</u> <i>L</i> ⁰	2307.6±0.6	2308.6 ± 0.5		
	$K\underline{L}^{1}$	$2322.3 {\pm} 0.8$	2323.7±0.4		
Cl ^d	<u>К</u> <u></u> 0	2621.9±0.8	2621.4±0.5	2621.9	
	$K\underline{L}^{1}$	2639.1±1.0	2640.4±0.5	2640.2 ± 1.4	
К	<u>К</u> <u>L</u> ⁰	3313.3±0.8	3314.1±1.0	3312.9	
	KL^{1}	3334.3±1.2	3335.1±0.9	3336.0 ± 3.2	
Ca	<i>Κ</i> <u>L</u> ⁰	3690.5±1.0			3690.0
	$K\underline{L}^{1}$	3713.0±2.0			3714.0

^aReference 1.

^bReference 11.

^cReference 12.

^dData reported earlier by the authors (Ref. 8).

	Present work	Demarest et al. ^a	Watson <i>et al.</i> ^b	Maurer <i>et al.</i> ^c Theory	
Element	Photon excitation	Heavy-ion excitation	Heavy-ion excitation	M electron number	Energy (eV)
Р	12.4±1.0	12.6±0.6		0	13.6
				1	13.2
				2	12.8
				3	12.4
				4	11.9
				5	11.6
S	14.7 ± 1.4	15.1±0.9		0	15.1
				1	14.7
				2	14.4
				3	13.9
				4	13.5
				5	13.1
				6	12.7
*Cl ^d	17.2 ± 1.8	19.0±1.0	18.3 ± 1.4	0	16.7
				1	16.3
				2	16.0
				3	15.5
				4	15.0
				5	14.7
				6	14.3
				7	13.9

TABLE IV. KL^{1} energy shifts from KL^{0} in electron volts.

^aReference 1.

^bReference 11.

^cReference 13.

^dData of Cl of KCl reported earlier by the authors (Ref 8).

general agreement of the present energy shifts with the theoretical estimations up to 3 to 4 M electrons present at the time of $K\alpha$ x-ray emission. In conclusion, in the present investigations systematic data on $K\alpha \underline{L}^{1}$ x-ray satellites in P, S, Cl, K, and Ca by photon excitation are reported perhaps for the first time.

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