The Extreme Ultraviolet Spectra of Scandium VI, Scandium VII and Other Elements Isoelectronic with Phosphorus I and Sulphur I*

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(Received July 6, 1937)

The spectra of Sc, Ti, V and Cr have been photographed in the region 80A to 700A with a large grazing incidence vacuum spectrograph. The irregular doublet law and constant second difference law have been used to aid in the identification of multiplets in ions of these elements. In the S I isoelectronic sequence, Sc VI multiplets involving the $3s^23p^4$ ^3P, ^1D, $^1S - 3s3p^5$ $^3P^0$; $3s^23p^34s$ $^3S^0$, $^{1, 3}D^0$, $^{1, 3}P^0$ terms and the Ti VII multiplet involving the $3s^23p^4$ $^3P - 3s3p^5$ $^3P^0$ terms have been observed. A number of intercombination lines have been identified, making possible an accurate calculation of the term values relative to the ground state. In the P I isoelectronic sequence, Sc VII multiplets involving the $3s^23p^3$ $^4S^0$, $^2D^0$, $^2P^0$ $-3s^23p^24s$ ^4P, ^2D, ^2P and $3s3p^4$ ^4P terms; Ti VIII multiplets involving the $3s^23p^3$ $^4S^0$, $^2D^0$, $^2P^0 - 3s^23p^24s$ ^4P, ^2P, ^2D terms; and V IX multiplets involving the $3s^23p^3$ $^4S^0$, $^2D^0 - 3s^23p^24s$ ^4P, ^2D terms have been observed. Since no intercombination lines have been observed it is impossible to assign relative term values to the doublet and quartet systems.

THE spectra of all ions of the first eight elements of the periodic table are well known. A great deal of work has been done also on the isoelectronic ions of elements following oxygen. However, previous to the beginning of the present investigation, the spectra of scandium were known only for Sc I, Sc II, Sc III, and Sc XI. This was undoubtedly due to the fact that the highly ionized spectra of scandium was very hard to excite. There was also a lack of information about the spectra of various ions of the neighboring elements Ti, V, and Cr, though these elements are not particularly hard to excite.

Other members of this laboratory have reported the work done on Sc IV,[1] Sc V,[2] Sc VIII, IX[3] and other neighboring ions in isoelectronic sequences related to these scandium ions. It is the purpose of this paper to present the results of the investigation of the spectra of Sc VI, Sc VII and related ions in the S I and P I isoelectronic sequences.

The spectra of the elements Sc, Ti, V, and Cr were photographed throughout the region 80 to 700A by means of a large grazing incidence vacuum spectrograph.[4] Titanium, vanadium, and chromium electrodes, made in the conventional way by inserting a piece of the metal into the hollow end of a $\frac{1}{4}$-inch diameter rod (Al or Cu) and wedging it fast, were used as the anode of a vacuum spark.

Satisfactory scandium electrodes were made by packing a mixture of four parts of scandium oxide and one part of boron oxide in a copper (Al) shell electrode and hardening the mixture by heating the electrode to a red heat in a small electric furnace.

The energy for excitation was supplied by a four kenotron bridge rectifier which charged a bank of condensers of 0.2 mf (0.45 mf) capacity, to 100 kv (40 kv).

Usually, copper lines from the copper shell of the electrodes were used as wave-length stand-
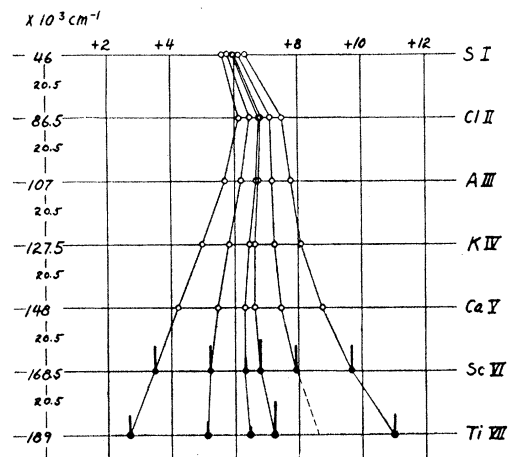
Fig. 1. Displaced frequency diagram. The $3s^23p^4$ ^3P $-3s3p^5$ $^3P^0$ multiplets of the sulphur I sequence.

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[1] Kruger, Weissberg and Phillips, Phys. Rev. 51, 1090 (1937).

[2] Kruger and Phillips, Phys. Rev. 51, 1087 (1937).

[3] Kruger and Phillips, Phys. Rev. 52, 97 (1937).

[4] Kruger, Rev. Sci. Inst. 4, 128 (1933).

TABLE I. *Multiplets in Scandium VI.*

$3s^23p^4$	$^3P_2$	$^3P_1$	$^3P_0$	$^1D_2$	$^1S_0$
TERM VALUES	0	3350	4476	21,397	49,238
$3s3p^5$					
$^3P_2{}^0$ 175,348	(5) 570.295 175,348	(4) 581.399 171,999			
$^3P_1{}^0$ 178,195	(4) 561.183 178,195	(4) 571.916 174,851	(2) 575.573 173,740		
$^3P_0{}^0$ 179,775		(4) 566.794 176,431			
$3s^23p^34s$					
$(^4S)\ ^3S_1{}^0$ 452,073	(30) 221.203 452,073	(6) 222.855 448,722	(2) 223.419 447,590		
$(^2D)\ ^3D_1{}^0$ 472,406	(0) 211.696 472,375	(4) 213.194 469,056	(5) 213.701 467,930		
$^3D_2{}^0$ 472,556	(5) 211.615 472,556	(8) 213.124 469,210			
$^3D_3{}^0$ 472,985	(15) 211.423 472,985				
$(^2D)\ ^1D_2{}^0$ 478,354	(1) 209.050 478,354	(1) 210.530 474,991		(15) 218.840 456,955	
$(^2P)\ ^3P_0{}^0$ 491,810		(4) 204.725 488,460			
$^3P_1{}^0$ 492,092	(2) 203.214 492,092	(2) 204.604 488,750	(4) 205.067 487,646		
$^3P_2{}^0$ 492,800	(6) 202.922 492,800	(5) 204.310 489,452		(1) 212.132 471,405	
$(^2P)\ ^1P_1{}^0$ 497,984	(1) 200.810 497,983	(494,634)*	(0) 202.638 493,491	(8) 209.826 476,585	(3) 222.844 448,744

* Masked by oxygen line.

ards,[5] but in the case of scandium, oxygen[6] lines excited from the oxide were used also. The exposures using aluminum shell electrodes were made in order to find any lines which might be masked by lines of the copper spectrum.

In the analysis of these spectra the regular

[5] Kruger and Cooper, Phys. Rev. **44**, 826 (1933).

[6] Edlen, Nova Acta Reg. Soc. Sci. Upsaliensis, Ser. IV, Vol. 9, No. 6 (1934).

doublet law, the irregular doublet law and corresponding displaced frequency diagrams, and the constant second difference law have been used. That the latter is applicable to cases where the total quantum number n changes by some integer a, can be seen from the following. If the term value is expressed by $T = R(Z-s)^2/n^2$ the radiated frequency is given by

$$\nu = T_1 - T_2 = \frac{R(Z-s_1)^2}{n_1{}^2} - \frac{R(Z-s_2)^2}{(n+a)^2},$$

which reduces to $\nu = c_1Z^2 + c_2Z + c_3$ where c_1, c_2 and c_3 are constants involving R, n, a and $s_{1,\,2}$. This expression is quadratic in Z, and explains the constant second differences between radiated frequencies when n changes by a, and provided there is no change in the screening constant in successive ions. Experimentally, the second differences vary by small amounts so that the screening constants must vary in a similar way.

SPECTRA OF IONS IN THE S I SEQUENCE

A major portion of an analysis of the spectra of the ions Sc VI, Ti VII, V VIII and Cr IX, in the S I isoelectronic sequence, had been completed when the commendable work of Edlen[7] appeared, giving an analysis of most of these spectra. Since Edlen's work agrees with our analysis, only that part of our analysis not duplicated by him is included here. This includes the spectra of Sc VI and one multiplet of Ti VII.

The normal electron configuration of scandium VI is $3s^23p^4$, which gives rise to the normal

[7] Bengt Edlen, Zeits. f. Physik **104**, 188 (1937).

FIG. 2. Displaced frequency diagram. Multiplets of the $3s^23p^4 - 3s^23p^34s$ transition in the sulphur sequence.

TABLE II. *Radiated frequencies with first and second differences for some of the strongest lines arising from transitions between the $3s^23p^4 - 3s^23p^34s$ configurations of the sulphur isoelectronic sequence.*

	$^3P_2 - {}^3S_1^0$			$^3P_2 - {}^3D_3^0$			$^1D_2 - {}^1D_2^0$		
	ν	FIRST DIFFERENCE	SECOND DIFFERENCE	ν	FIRST DIFFERENCE	SECOND DIFFERENCE	ν	FIRST DIFFERENCE	SECOND DIFFERENCE
S I	55331			67843			60000		
		57274			58939			(58000)	
Cl II	112605		10799	126782		10961	(118000)		(10308)
		68073			69900			(68308)	
A III	180678		(11549)	196682		11404	186308		(11373)
		(79622)			81304			79681	
K IV	(260300)		(10992)	277986		10669	265989		10212
		(90614)			91973			89893	
Ca V	350914		(10545)	369959		11053	355882		11180
		101159			103026			101073	
Sc VI	452073		11008	472985		10989	456955		10782
		112167			114015			111855	
Ti VII	564240		10843	587000		10975	568810		10645
		123010			124990			122500	
V VIII	687250		10890	711990		10890	691310		10640
		133900			135880			133140	
Cr IX	821150		10940	847870		10430	824450		10750
		144840			146310			143890	
Mn X	965990		10440	994180		11960	968340		10050
		155280			158270			153940	
Fe XI	1121270			1152450			1122280		

states ^3P, ^1D and ^1S. The ^3P term is the ground state and above this are the ^1D and ^1S in the order named. The ^3P term is inverted. Above the normal states are the excited states $^3P^0$ and $^1P^0$ arising from the $3s3p^5$ electron configuration. The $3s3p^5\ {}^3P^0$ term is also inverted. The next excited states above these should be $^{3,\ 5}S^0$, $^{1,\ 3}D^0$ and $^{1,\ 3}P^0$ arising from the $3s^23p^34s$ electron configuration. All terms arising from this configuration are normal.

In the analysis of the spectrum, radiations involving transitions from all excited states, except the $3s3p^5\ {}^1P^0$ and the $3s^23p^34s\ {}^5S^0$, to the normal states have been found. Table I gives the intensity, wave-length, frequency and classification of all the spectral lines identified, together with the term values of the energy levels. All intermultiplet separations have been checked experimentally wherever possible. All other multiplet separations which are involved in only one transition, have been checked for agreement with the regular doublet law. A number of intercombination lines have been identified; thus it is possible to give accurately the relative term values of all the levels, with respect to the $3s^23p^4\ {}^3P_2$ level as zero.

The relation of the multiplets of Sc VI to similar multiplets of the sulphur isoelectronic sequence is shown in the displaced frequency graphs, Figs. 1 and 2. Fig. 1 is a constant first difference graph for the $3s^23p^4\ {}^3P - 3s3p^5\ {}^3P^0$ multiplet and follows the irregular doublet law. Fig. 2 is a constant second difference graph and illustrates the constant second difference law. The regularity of the second differences is apparent in Fig. 2, and is further illustrated in Table II where the frequencies, and first and second differences for some of the strong lines arising from transitions between the $3s^23p^4 - 3s^23p^34s$ configurations are tabulated.

The data for S I, Cl II, A III, K IV and Ca V are available in the literature.[8-11] The data for

TABLE III. *The $3s^23p^4\ {}^3P - 3s3p^5\ {}^3P^0$ multiplet of titanium VII.*

$3s^23p^4$		$^3P_2$	$^3P_1$	$^3P_0$
	TERM VALUES	0	4535	5893
$3s3p^5$				
$^3P_2^0$	196,264	(12) 509.518 196,264	(5) 521.561 191,732	
$^3P_1^0$	200,060	(6) 499.850 200,060	(2) 511.444 195,525	(3) 515.021 194,167
$^3P_0^0$	(202,198)		(197,663)*	

* Obscured by second-order titanium line.

[8] J. E. Ruedy (S I), Phys. Rev. 44, 757 (1933).
[9] K. Murakawa (Cl II), Zeits. f. Physik 96, 117 (1935).
[10] J. C. Boyce (A III, IV), Phys. Rev. 48, 396 (1935).
[11] I. S. Bowen (K V, VI; Ca VI, VII), Phys. Rev. 46, 791 (1934).

Ti VII, V VIII, Cr IX, Mn X and Fe XI are to be found in Edlen's publication,[7] except for the $3s^23p^4\,^3P-3s3p^5\,^3P^0$ multiplet of Ti VII. The intensities, wave-lengths and frequencies of the lines in thus multiplet are given in Table III. The $^3P_1-{}^3P_0{}^0$ line of this multiplet was obscured by the second order of an intense titanium line of frequency 395,318 cm⁻¹. The value given for

TABLE IV. *Multiplets in scandium VII.*

$3s^23p^3$		$^4S^0_{3/2}$	$^2D^0_{5/2}$	$^2D^0_{3/2}$	$^2P^0_{1/2}$	$^2P^0_{3/2}$
	SEPARATIONS		678		910	
$3s3p^4$ $^4P_{5/2}$		(4) 571.256 175,053				
$^4P_{3/2}$	2710	(3) 562.547 177,763				
$^4P_{1/2}$	1441	(2) 558.023 179,204				
$3s^23p^24s$ $(^3P)\,{}^4P_{1/2}$		(7) 184.607 541,691				
$^4P_{3/2}$	(1950)					
$^4P_{5/2}$	(2818)	(543,650)* (12) 182.993 546,469				
$(^3P)\,{}^2P_{1/2}$		(8) 191.602 521,916			(2) 199.163 502,101	(1) 199.524 501,193
$^2P_{3/2}$	3276			(8) 190.654 524,511	(1) 197.871 505,380	(5) 198.229 504,467
$(^1D)\,{}^2D_{5/2}$		(525,192) (1) 185.375 538,866	(10) 185.808 538,190			(15) 193.000 518,135
$^2D_{3/2}$	142	(7) 185.526 539,008		(538,330)	(8) 192.607 519,192	(518,282)*

* Masked by oxygen line.

TABLE V. *Multiplets in titanium VIII.*

$3s^23p^3$		$^4S^0_{3/2}$	$^2D^0_{3/2}$	$^2D^0_{5/2}$	$^2P^0_{1/2}$	$^2P^0_{3/2}$
	SEPARATIONS		1077		1456	
$3s^23p^24s$ $(^3P)\,{}^4P_{1/2}$		(10) 151.485 660 130				
$^4P_{3/2}$	2719	(20) 150.864 662,849				
$^4P_{5/2}$	3653	(20) 150.037 666,502				
$(^3P)\,{}^2P_{1/2}$		(5) 156.442 639,215			(1) 162.019 617,212	(0) 162,401 615,760
$^2P_{3/2}$	4234		(10) 155.673 642,372		(0) 160.914 621,450	(4) 161.293 619,990
$(^1D)\,{}^2D_{5/2}$		(1) 151.915 658,263	(20) 152.164 657,186			(3) 151.527 634,812
$^2D_{3/2}$	227	(8) 151.863 658,488		(657,411)	(3) 157.107 636,509	(2) 157.470 635,042

TABLE VI. *Multiplets in vanadium IX.*

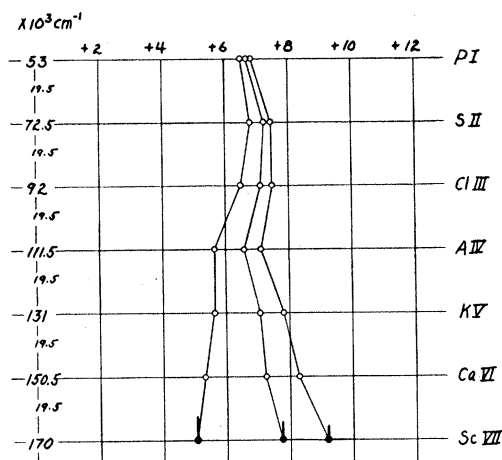| $3s^23p^3$		$^4S^0_{3/2}$	$^2D^0_{3/2}$	$^2D^0_{5/2}$
	SEPARATIONS			1523
$3s^23p^24s$ $(^3P)\,{}^4P_{1/2}$		(5) 126.732 789,066		
$^4P_{3/2}$	3630	(8) 126.152 792,696		
$^4P_{5/2}$	4625	(12) 125.420 797,321		
$(^1D)\,{}^2D_{5/2}$			(0) 126.810 788,501	(10) 127.068 786,978
$^2D_{3/2}$	358		(5) 126.765 788,859	(787,336)

FIG. 3. Displaced frequency diagram. The $3s^23p^3\,{}^4S^0$ $-3s3p^4\,{}^4P$ multiplet of the phosphorus sequence.

this line in Table III was that predicted by the regular doublet law, as applied to the $3s3p^5\,{}^3P_0{}^0$ $-{}^3P_1{}^0$ separation in successive ions of the sequence.

THE SPECTRA OF IONS OF THE P I SEQUENCE

The ions Sc VII, Ti VIII and V IX are isoelectronic with phosphorus. The normal electron configuration of these ions is $3s^23p^3$, which gives rise to the normal states $^4S^0$, $^2D^0$ and $^2P^0$. The $^4S^0$ is the ground state, above which are the $^2D^0$ and $^2P^0$ states respectively. The first excited states are $^2,\,{}^4P$, ^2D and ^2S arising from the $3s3p^4$ configuration. The ^4P term is inverted,
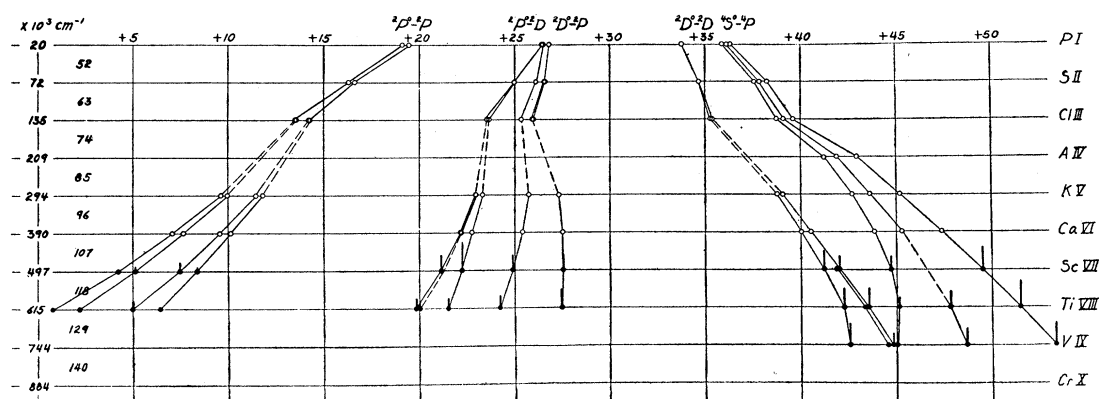
$\times 10^3\,cm^{-1}$

FIG. 4. Displaced frequency diagram. Multiplets of the $3s^23p^3-3s^23p^24s$ transition in the phosphorus sequence.

as it should be. The next excited states above these are [2,] ^4P, ^2D and ^2S arising from the $3s^23p^24s$ configuration. The ^4P and the ^2P terms are normal but the ^2D term is inverted in all the ions of the sequence.

In the analysis of the spectra of the ions Sc VII, Ti VIII and V IX, the $3s^23p^3$ $^4S^0$ $-3s3p^4$ ^4P multiplet has been identified in Sc VII only. No multiplets involving the $3s3p^4$ ^2D, ^2P and ^2S terms appear on our spectrograms. Multiplets involving the transitions $3s^23p^3$ $^4S^0$ $-3s^23p^24s$ ^4P and $3s^23p^3$ $^2D^0$, $^2P^0-3s^23p^24s$ ^2P, ^2D have been found in Sc VII and Ti VIII. The term value of the $3s^23p^24s$ ^2S term is not known for any ion of the phosphorus sequence.

An attempt was made to extend the identification of the radiations of the P I-like ions into V IX, but only the lines belonging to the $3s^23p^3$ $^4S^0-3s^23p^24s$ ^4P and to the $3s^23p^3$ $^2D^0$ $-3s^23p^24s$ ^2D multiplets were identified. The other multiplets did not appear on our spectrograms.

The intensity, wave-length, frequency and classification of all the lines identified in Sc VII, Ti VIII and V IX are given in Tables IV, V and

VI, respectively. Some of the weaker lines of the multiplets are missing or obscured by oxygen lines, but fortunately the doublet separations could still be checked experimentally, making positive identification possible. The separations of the ^4P terms have been checked for agreement with the regular doublet law.[12] Unfortunately no intercombination lines have been identified, hence it is not possible to assign term values to any of the doublet terms relative to the $^4S^0$ ground state.

The relation of the multiplets of Sc VII, Ti VIII and V IX to similar multiplets of ions isoelectronic with phosphorus is shown in the displaced frequency graphs, Figs. 3 and 4. Fig. 3 is a constant first difference graph for the $3s^23p^3$ $^4S^0-3s3p^4$ ^4P multiplet, while Fig. 4 is a constant second difference graph for multiplets arising from transitions between terms of the $3s^23p^3$ and the $3s^23p^24s$ configurations. The data for the ions P I, S II, Cl III, A IV, K V and Ca VI are available in the literature.[10, 11, 13-15]

[12] Gibbs and White, Phys. Rev. 29, 655 (1927).
[13] H. A. Robinson (P I), Phys. Rev. 49, 297 (1936).
[14] S. B. Ingram (S II), Phys. Rev. 32, 172 (1928).
[15] I. S. Bowen (Cl III), Phys. Rev. 31, 34 (1928).