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ON THE SPARK SPECTRA OF LEAD

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The spectrum of Lead has been the object of many investigations. Yet until recently little progress has been made in the identification of series relationships in the arc and spark spectra of the element. This element is the chemical analogue of C, Si, Ge and Sn; and since it has the same number and type of outer electrons its spectral structures may be expected, according to present-day theories, to resemble those of the abovementioned elements. Such resemblances between homologous spectra are often very close, though there are occasionally minor but significant differences, which may perhaps prove of importance in the refinement of modern atomic theories. Recently through the work of Thorsen¹, Grotrian², Sur³ and McLennan⁴, a distinct advance was made in the analysis of the arc spectrum of Lead. The first spark spectrum of the element was investigated by Geissler.⁵

The preliminary attempts at the classifications of the second and third spark spectra of Lead, from the existing lists of published wavelengths was seriously handicapped by the lack of descriptive data. Descriptions of arc and spark spectra of the element in limited wavelength intervals have been published by various observers. The most reliable ones up to the year 1911 are quoted by Kayser in Volume VI of the *Handbuch der Spectroscopie*. They are by Kayser and Runge⁶ (arc spectrum 2085 to 6002-A.U.), by Thalen⁷ (spark spectrum 4058 to 6656 A.U.), by Exner and Haschek⁸ (arc spectrum 2237 to 6002 A.U., and spark spectrum 2170 to 4572 A.U.), and by Eder and Valenta⁹ (arc spectrum 5609 to 7229 A.U., and spark spectrum 4272 to 6793 and 2088 to 2733 A.U.). Since the appearance of this work in 1912 the spectrum of this element has been reinvestigated by Klein¹⁰, with greater accuracy by using a 20 feet concave Grating Spectrograph. All the abovementioned measures were based on Rowland's system of standard wavelengths. In addition to these, contributions to the spectra of Lead have been made by Kimura and Nikumura¹¹, who, by photographing the cathode spectrum grouped some of the important lines under successive stages. No attempts were made by these authors to measure the wavelengths accurately. Only after the present work was begun was the writer able to procure a paper published by S. Smith¹², who photographed by means of a two-metre concave grating, the vacuum spark between electrodes of the metal, in the region 2400 A to 4800 A. It is found however that the hot spark does not give the highest members of spark lines, which I have been able to photograph with the highest excitation in the condensed spark. This is clearly seen from an examination of the writer's spectrograms (plates II and IV).

The measurements till now available are not sufficient for a complete analysis of the spark spectrum of Lead, since it is desirable to know the degrees of excitation at which the various lines appear and also to know the character of the spectrum lines, i.e., their sharpness, diffuseness, etc. The experiments of the writer were therefore aimed at photographing the whole region 2050 to 7000 A, with higher dispersion and

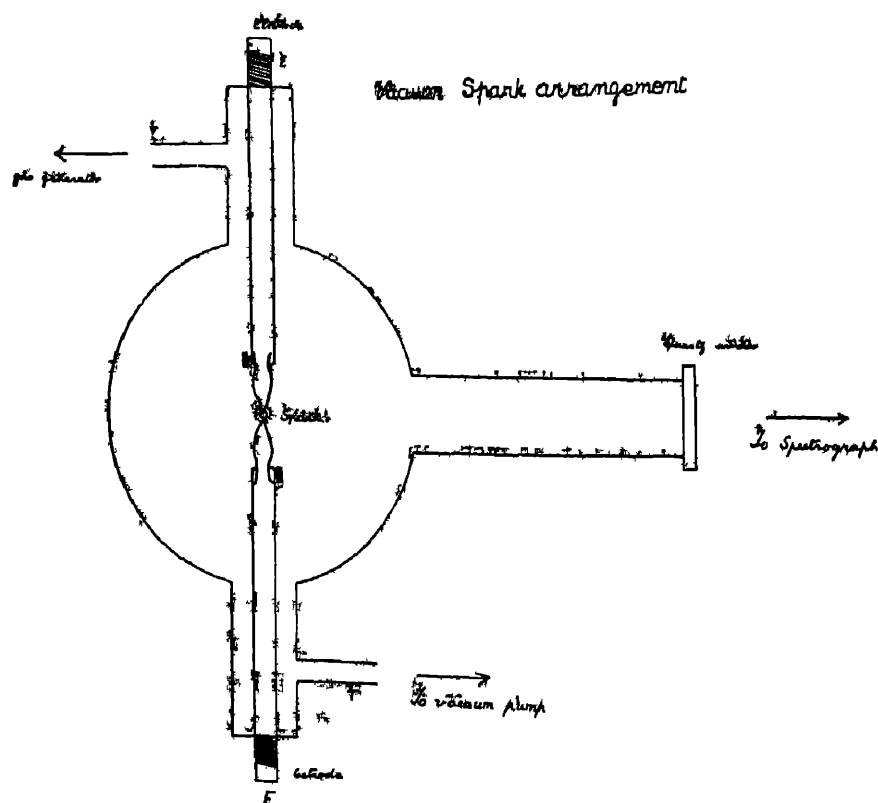
under different degrees of excitation as a preliminary to the analysis of the higher spark spectra. The results show that the procedure is justified many additional lines having been discovered in this work. The new observations of the spark spectrum together with the lines which have been classified in the spectra of Pb III and Pb IV are presented in this paper. In addition to the accurate measurement of wavelengths attempts have been made in this investigation to improve upon the earlier descriptions by making a careful selection of the lines characterising Pb I, Pb II, Pb III and Pb IV. This critical differentiation of lines belonging to different stages is generally made by photographing the spectrum under varying degrees of discharge.

To provide data likely to be useful in identifying the spectra of higher stages of ionisation a study was made of the spark spectrum of pure Lead in air in vacuo and in an atmosphere of hydrogen at varying pressures and also of the arc in vacuum between electrodes of the pure metal. The spark was produced by a $\frac{1}{2}$ kilo watt 20000 volt transformer. The secondary contained a battery of large plate condensers of capacity 0.03 mfd (constructed for the purpose) in parallel with the spark gap in the experimental chamber. To distinguish lines due to different stages of ionisation the spectrum was photographed under varying degrees of discharge which is done by including in the secondary circuit a variable self inductance and capacity.

Description of apparatus

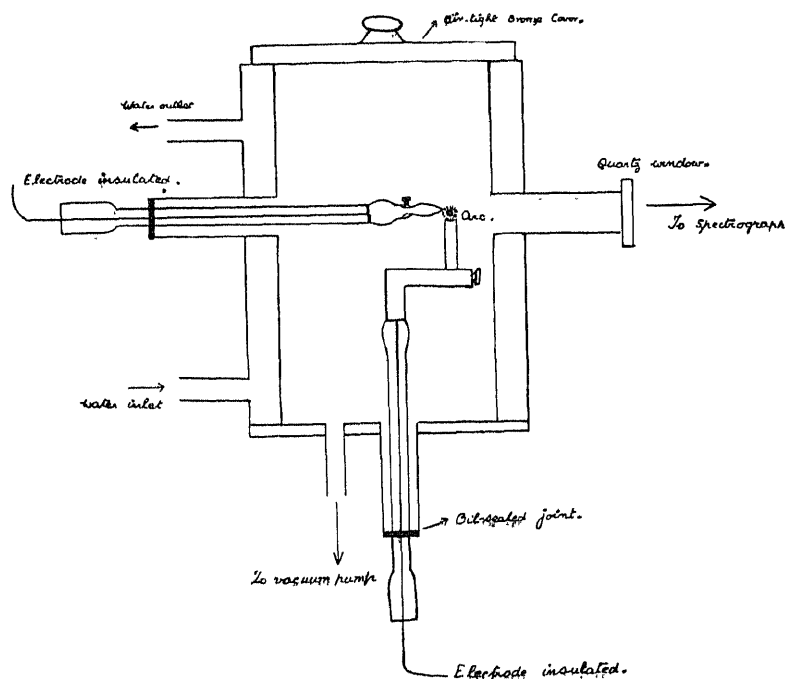
Sources of radiation — The apparatus used for the study of the spark spectrum is shown in diagram 1. It consists of a pyrex bulb capacity about one litre with side openings EI through which the electrodes pass. To the ends of these small pieces of metal can be fixed. A plane plate of quartz is attached to the end of the long projecting tube and serves as a window through which the spectrum of the spark is photographed. The two side tubulures (TT) are intended for filling the flask with hydrogen. Pure hydrogen gas from a generator after passing through drying agents is passed through the flask for nearly 30 minutes, thereby driving the last traces of air from the flask. By connecting the flask then to an air pump the flask could be exhausted to any desired pressure and the spark spectrum photographed.

FIG 1



The spectrum of the vacuum arc of the metal was photographed, using a specially constructed arc lamp as the source of radiation. A diagrammatic sketch of the vacuum arc is given to Figure II. It consists of a double-walled cylindrical vessel fitted with a vacuum joint for one electrode and an aperture opposite for light to emerge. The second electrode passes through a similar joint in the base of the lamp and the clip for the specimen is arranged so that the arc is struck as close as possible to the window, without arcing to the wall taking place. The lid of the vacuum chamber is a bronze disc, which has been ground to make a tight joint which can be sealed with suitable vacuum wax or grease. Connection to the vacuum pump is made through the base of the lamp and nozzles are provided so that the cylindrical wall may be kept cool with circulating water. Each electrode consists of a brass tube passing through a gland and having an insulated wire passing through it. Electrical connection is made to the terminal situated on the ebonite handle, provided for the manipulation of the arc. The glands have been filled with vacuum grease for maintaining a vacuum. The lamp operates steadily with currents varying from 4 to 6 amps.

FIG. II.



Spectrographs employed.—The spectrograms were obtained in the first and second order of a 4-inch concave grating, of 10 feet radius of curvature in eagle mounting. These were supplemented by several plates taken with a Hilger H_2 Quartz spectrograph, which is used not only to record the faint lines in the ultra-violet, but also for wavelength measurements in the region 2550 to 2050-A. In this region this spectrograph compares favourably in dispersion and resolving power with the concave grating spectrograph and at the same time, has a good light gathering power. Comparison spectra of the iron arc are impressed on the plates after each of the exposures. The spectrograms are obtained on photographic plates of thin glass which could be bent to the focal curves of the spectrographs. The region 3600 to 6500-A was also visually examined, with a view to study the behaviour of the lines under different conditions of excitation, by a constant deviation spectrograph. For photographing the region below 2500-A, the plates were sensitized in the manner described in Volume II of Baly's Spectroscopy, with comptoneter oil. The exposure times ranged, in the case of the concave grating spectrograph from 10 to 30 minutes, while in the case of the quartz spectrograph, up to 2500-A, the times ranged from 5 to 10 minutes and in the region 2500 to 2050-A exposures of 15 to 30 minutes were given.

Method of wavelength determination—All plates were measured in two directions with a Hilger comparator and the wave length measurements were made relative to International Secondary Standards in the spectrum of the iron arc. For the region below 3370 Å the iron arc wavelengths published by Burns were used. In the case of the prism spectrograms the wavelengths were calculated by means of Hartman's dispersion formula $\lambda = \lambda_0 + \frac{c}{n}$ where λ_0 , c and n are constants determined from the comparison spectrum and n the distance of the unknown line from a fixed point of reference on the plate. Spectrograms obtained with the grating are measured by using a linear scale.

Intensity estimates were made directly from the plates as viewed in the measuring microscope on a scale of 0 to 10. The vacuum wave numbers corresponding to the observed wavelengths are taken from Kayser's *Tabelle der Schwingungszahlen* and are given in column 3 of Table I. In column 1 are given the observed wavelengths in Å. In column 2 are given the intensity estimates in column 4 the stages of ionisation of the prominent lines and in column 5 are given the lines classified in this investigation. The symbols accompanying the intensity values have the following meanings—

s = sharp d = diffuse bd = broad and diffuse and dd = very diffuse

TABLE I

Wavelength (Å.)	Int	W number cm^{-1}	St g and lass fi ta n	W (Å)	Int	W number m^{-1}	Stage nd lassfi ation
655.82	3	152439	IV 6 D-7p P	1439.2	1d	69478	IV 6 D ₂ -6p F ₂
760.90	0	131420	IV 6 D-7p P	1553.1	20	64387	III 1 S -1 P
804.55	1	124293	IV 6 D-7p P	1597.8	0	62586	III 1 P -1 D ₂
884.98	6	112997	IV 6 D ₂ -7p P	1610.1	1	62107	III 1 P -1 D
908.54	5	110067	IV 1 P-2 S	1711.1	4	58442	III 1 P -1 D ₂
922.5	4	108401	IV 1 P-1 D	1749.9	1	57146	IV 6 D ₂ -6p F
979.47	2	102096	IV 6 D ₂ -7p D ₂	1826.2	0	54759	III 1 P -1 S
995.8	2	100422	III 1 P-1 P				
1028.7	10	97210	IV 1 S-1 P	2060.43	3	48518.0	
1030.5	3	97040	III 1 P-1 D	2088.55	2	47864.8	I
1043.9	12	95338	III 1 S-1 P	2104.41	2dd	47504.1	
1059.3	1	94400	IV 6 P-7p P	2107.73	5dd	47429.3	
1069.2	2	93528	III 1 P-1 D	2110.75	3	47361.5	
1074.7	3	93049	III 1 P-1 D	2114.98	1dd	47266.8	I
1087.34	2	91968	IV 6 D ₂ -7p P	2192.21	3s	46884.8	
1096.5	1d	91189	IV 6 D-7p D	2142.83	5s	46652.5	
1103.6	0d	90613	IV 6 D-6p D	2152.64	4	46439.9	
1104.8	0d	90510	IV 6 D ₂ -6p F	2169.86	10bd	46071.4	
1115.0	2	89686	III 1 P-1 S	2174.61	0dd	45970.8	
1116.2	4	89590	IV 1 P-1 D	2178.72	1s	45884.1	
1118.6	3	89397	III 1 P-1 D	2189.76	6	45652.8	I
1123.45	3	89012	IV 1 P ₂ -2 S	2192.43	2	45597.2	
1142.9	1	87497	III 1 P-1 P	2203.62	8dd	45365.7	II
1145.0	3	87336	IV 1 P-1 D	2218.21	3	45067.3	I
1165.1	4	85830	III 1 P-1 P	2237.48	8b	44679.2	I
1167.0	4	85690	III 1 P-1 S	2242.67	5	44575.8	
1231.3	1	81215	III 1 P-1 P	2246.83	10bd	44493.3	I
1233.6	3	81068	IV 6 D ₂ -7p D	2254.13	3dd	44349.2	I
1250.6	4	79962	III 1 P ₂ -1 D	2259.76	0dd	44238.8	
1266.9	1	78933	III 1 P ₂ -1 D	2264.73	1s	44141.7	
1274.6	0	78456	III 1 P ₂ -1 D	2276.58	3s	43911.9	
1279.5	3	78167	IV 6 D-6p F	2280.51	1s	43886.3	
1308.2	2	76441	IV 6 D-6p D	2287.52	1bd	43702.0	
1315.2	9	76150	IV 1 S-2 P	2290.17	0dd	43651.4	
1323.2	0	73981	IV 6 S ₂ -7p P	2293.02	1bd	43597.1	
1371.3	3	72897	III 1 P ₂ -1 P	2294.16	0	43575.5	
1409.6	2	71093	III 1 P-1 S	2296.65	2	43528.2	
1477.1	1d	69585	IV 6 S ₂ -6p D	2300.35	4s	43458.2	IV 2 P -3 S

TABLE I—cont.

Wavelength (I.A.)	Int.	Wave number in cm^{-1}	Stage and classification.	Wavelength (I.A.)	Int.	Wave number in cm^{-1}	Stage and classification.
2308.12	0bd	43312.7		2868.19	3	34855.0	
2312.70	0d	43226.2		2873.33	10	34792.6	I.
2317.45	2dd	43137.6		2937.55	4	34032.0	IV $2^2P_2-2^2D_2$.
2332.48	8bd	42859.7	I.	2949.45	9dd	33894.7	II.
2343.72	1s	42654.1		2977.98	9	33570.0	I.
2353.91	0d	42469.5		3002.65	5s	33294.2	II.
2360.19	1dd	42356.5		3010.19	3s	33210.8	
2368.54	2d	42207.2		3016.63	8dd	33133.0	II.
2370.27	0s	42176.4		3025.55	2d	33042.3	
2382.28	3s	41963.8		3028.77	2	33007.1	
2386.01	2s	41898.2		3031.68	4s	32975.5	IV.
2389.12	4s	41843.6	I.	3043.90	10	32843.1	III $1^3D_1-1^3F_2$.
2393.88	7dd	41760.5		3052.64	10	32749.0	IV.
2399.76	3s	41658.1		3056.84	4	32704.0	IV $1^2D_2-2^2P_2$.
2402.16	7bd	41649.3	I.	3062.42	4	32644.5	
2411.79	6bd	41450.4	I.	3071.54	4	32547.5	
2416.13	0	41375.9		3087.13	5	32383.2	IV.
2418.78	0	41330.6		3089.17	7	32361.8	III $1^2D_2-1^3F_2$.
2424.21	0	41238.0		3103.00	4	32217.6	III.
2428.70	8bd	41161.8	IV $2^2P_1-2^2D_2$.	3109.27	2	32152.6	
2433.65	2s	41078.1		3118.17	5	32060.8	I.
2443.91	10bd	40905.6		3129.62	4	31943.5	III.
2446.30	10bd	40865.7	I.	3137.87	10	31859.5	III $1^3D_2-1^3F_3$.
2463.21	2	40585.2		3145.70	4	31780.3	III.
2476.38	9	40369.3		3176.59	10	31471.2	III $1^3D_3-1^3F_4$.
2478.63	3	40332.7		3191.49	1	31324.3	III $1^3D_3-1^3F_2$.
2494.07	2d	40083.0		3214.82	0	31097.0	
2495.61	3d	40058.3		3221.00	10	31037.3	IV $2^2S_1-2^2P_2$.
2497.16	2s	40033.4		3227.16	3	30978.1	IV.
2508.87	2	39846.6		3231.31	3	30938.3	
2527.06	3dd	39559.8	II.	3240.21	9	30853.3	I.
2533.38	3dd	39461.1	IV.	3242.95	9	30827.3	III $2^2D_3-2^2F_3$.
2534.81	3dd	39438.8	IV.	3247.70	2	30782.2	
2562.37	10	39014.7	III.	3262.41	3	30643.4	I.
2568.48	6	38921.9	IV.	3276.15	9	30514.9	III $2^2P_1-2^2D_2$.
2577.34	8	38788.1	II.	3279.30	9	30485.6	III.
2613.78	10	38247.4		3280.09	9	30478.2	IV $1^3D_3-2^2P_1$.
2614.28	5	38240.0	I.	3298.04	9	30313.3	III $2^2P_1-2^2D_1$.
2623.37	6	38035.1	I.	3309.22	8d	30209.9	
2637.81	3	37899.0		3360.40	4s	29749.8	
2638.53	3	37888.6	II.	3361.59	4s	29739.3	
2640.51	3s	37860.2		3365.93	5s	29701.0	
2650.33	6dd	37719.9		3437.15	2s	29085.6	III.
2657.15	4s	37623.1	I.	3452.17	6d	28950.0	II.
2663.23	10	37537.2	I.	3455.18	8d	28933.8	III.
2697.60	5d	37059.0		3476.27	0	28758.3	
2712.81	0	36851.2		3483.46	9	28698.9	III $1^3F_3-1^3G_4$.
2717.38	6d	36789.3	II.	3505.37	3d	28519.5	III $1^3F_4-1^3G_6$.
2719.97	3d	36754.2	II.	3530.39	3	28317.4	
2733.23	2	36575.9	I.	3534.06	3d	28288.0	
2734.58	2	36557.9	I.	3560.75	6	28076.0	III $1^1D_2-1^1F_3$.
2737.00	2	36525.6	I.	3563.06	4	28057.8	III $1^3F_4-1^3G_4$.
2740.87	2	36474.0		3565.26	1	28040.5	
2745.51	4	36412.4		3567.16	3	28025.5	III $1^1D_2-\beta$.
2752.15	1	36324.5	IV $2^2P_2-3^2S_1$.	3572.79	10s	27981.4	
2755.81	0	36276.3		3586.29	5d	27876.0	
2802.00	10	35678.3	I.	3589.81	7d	27848.7	III $1^3F_3-1^3G_7$.
2823.25	10	35409.8	I.	3592.95	6s	27824.4	IV $2^2D_3-2^2F_3$.
2833.12	10	35286.4		3621.10	1s	27608.1	
2864.45	10	34900.5	IV $2^2P_2-2^2D_3$.	3639.66	10s	27467.3	I.

TABLE I—cont

Wavelength (I A)	Int	Wave number in cm ⁻¹	Stage and classification	Wavelength (I A)	Int	Wave number in cm ⁻¹	Stage and classification
3648 61	1bd	27400 1		4534 54	3d	22046 8	
3655 56	8d	27347 8	III 1 ³ F ₂ —1 ³ G ₃	4571 45	7s	21868 8	III 2 ³ P ₂ —2 ³ S ₁
3665 64	0	27272 6	III	4605 28	3sd	21708 1	
3671 48	10d	27229 3	I	4630 38	5s	21585 8	
3674 75	4	27205 0	III 1 ³ F ₄ —1 ³ G ₃	4761 00	8s	20998 1	III 1 ³ S ₁ —2 ³ P ₁
3683 57	10s	27139 9		4798 27	6s	20835 6	III 1 ³ S ₁ —2 ³ P ₀
3689 22	8s	27098 2	III 1 ³ S ₁ —2 ³ P ₁	4802 18	6s	20818 1	
3699 52	0bd	27022 9		4827 15	0	20710 4	III 2 ¹ P ₁ —2 ³ S ₂
3706 22	3d	26974 0	III 2 ³ P ₀ —2 ³ S ₁	4855 20	1	20590 7	
3714 10	5dd	26916 8	II	4885 71	1	20462 2	
3719 30	2dd	26879 2		4941 12	1d	20232 7	
3729 06	4	26808 8	III 2 ³ P ₁ —2 ³ S ₁	5008 59	3s	19980 1	III 2 ³ P ₁ —α
3735 98	7	26759 2		5005 68	6s	19971 8	
3740 13	10s	26729 5		5043 21	10	19823 1	II
3749 22	1	26664 7		5062 91	3s	19746 0	III 1 ³ D ₂ —2 ³ P ₁
3786 20	8d	26404 2	II	5066 24	3s	19733 0	
3827 66	8d	26118 2	III 2 ³ P ₁ —2 ³ D ₂	5117 31	2sd	19536 1	
3882 94	10s	26082 3	III 2 ³ P ₁ —α	5139 42	2s	19452 0	
3841 83	10d	26021 9	III 2 ³ P ₂ —2 ³ D ₃	5163 75	6s	19360 4	IV
3854 11	10s	25989 0	III 1 ³ S ₁ —2 ³ P ₂	5192 29	6s	19253 0	III 1 ³ D ₁ —2 ³ P ₁
3873 22	1s	25811 0	IV	5201 65	6s	19219 3	
3909 29	5d	25572 9	IV 1 ³ D ₂ —2 ³ P ₁	5207 17	6d	19199 0	III 1 ³ P ₁ —2 ³ P ₁
3927 74	3b	25452 8		5220 42	2dd	19150 2	
3943 79	1ss	25349 2		5252 33	3d	19033 9	III 1 ³ P ₁ —2 ³ P ₀
3952 11	8d	25295 8	III 1 ³ F ₀ —2 ³ P ₀	5274 51	4s	18953 8	IV
3962 58	8s	25229 3		5372 65	10	18607 6	II
3994 98	1s	25024 1		5471 80	1	18270 5	II
4004 35	3s	24965 8		5496 61	1s	18188 0	
4019 65	8s	24870 8	I	5523 50	5s	18099 4	III 1 ³ D ₂ —2 ³ P ₂
4031 48	3d	24797 3		5544 60	1	18090 6	
4041 51	1	24736 3		5545 11	10	18028 9	II
4049 88	7s	24685 1		5609 18	10	17823 0	II
4058 01	10dd	24635 8	I	5664 49	3s	17649 0	
4062 22	8s	24610 2	I	5677 53	3s	17608 4	
4077 51	0db	24517 9		5678 89	3s	17604 2	
4095 04	2d	24412 9		5707 67	2s	17515 4	
4128 34	2d	24216 0	III	5779 75	4s	17297 0	III 1 ³ D ₂ —2 ³ P ₁
4141 56	3b	24138 7	III 1 ³ P ₁ —2 ³ P ₂	5828 12	3sd	17153 4	
4153 99	3db	24066 5		5857 59	6s	17067 1	III 1 ³ D ₂ —2 ³ P ₂
4168 05	7s	23985 3	I	5876 65	7d	17011 8	II
4174 38	4s	23948 9	III 1 ³ D ₁ —1 ³ F ₃	5890 33	6s	16972 3	
4182 40	8s	23903 0	IV 2 ³ S ₁ —2 ³ P ₁	5893 01	6s	16964 6	
4242 50	3dd	23564 4	II	5930 31	2s	16857 9	
4245 47	10	23547 6	II	5941 05	2s	16827 4	
4272 64	8s	23393 2	III 1 ³ D ₂ —2 ³ P ₁	6002 13	5s	16656 1	
4386 89	10	22788 3	II	6039 12	5s	16554 1	
4400 95	3s	22716 0	III	6081 81	3dd	16437 9	II
4447 10	3d	22489 3		6379 98	1	15669 7	
4496 12	3s	22235 2	III 1 ³ D ₂ —2 ³ P ₂	6660 15	8s	15010 5	II
4499 78	2	22217 3		6792 94	3s	14717 1	II

In addition to the spectrograms and wavelength measures obtained by the author, the wavelengths of Carrol and Mack have been used for the region 2100 Å.

Spectrum of Pb III

From the position of Pb in the table of elements it must be expected that the second spark spectrum consists of singlets and triplets and that the structure resembles generally that of the chemically analogous atom or ion O III, Si III, Ge III, and Sn III, Al II, Ga II, In II and Tl II. All these, except Pb III, are

Pb IV, have already been analysed. The present work on Pb III, Pb IV, therefore completes our knowledge of the series regularities in the spark spectra of elements of the fourth group. According to the theory of spectra developed by Pauli-Heisenberg, Russel and Hund, the characteristic terms arising out of any electronic configuration can be predicted with certainty and it will be seen that the results of the analysis of these spark spectra are in complete agreement with the theoretical predictions. The structure diagram of doubly ionised Lead may be written in the following manner :—

TABLE II.

K
2
L ₁ L ₂
2 6
M ₁ M ₂ M ₃
2 6 10
N ₁ N ₂ N ₃ N ₄
2 6 10 14
O ₁ O ₂ O ₃ O ₄ ...
2 6 10
P ₁ P ₂ P ₃ ...
2
Q ₁ Q ₂ ...

There are two electrons outside the complete spectroscopically neutral shells, which alone are effective in producing the optical spectrum. The most stable structure is that in which the two valency electrons are in the P₁ level. The spectroscopic term corresponding to this configuration is ¹S₀. Other less stable configurations and their characteristic terms are obtained by keeping one of the electrons in the P₁ orbit and allowing the other to run through the orbits P₂, Q₁, O₄, etc. The terms that these different electron configuration give rise to, may be predicted by the Hund Theory and are shown in the following table :—

TABLE III.

Electron configuration.	Terms predicted.	Terms observed.
2 P ₁	¹ S ₀	¹ S
1P ₁ 1P ₂	¹ S ₁ , ² S ₀	¹ S, ² S
1P ₁ 1Q ₁	¹ S ₁ , ² S ₀	¹ S, ² S
1P ₁ 1O ₄	a ³ F, a ¹ F	...
1P ₁ 1P ₃	¹ S ₁ , ² S ₀	¹ S, ² S
1P ₁ 1Q ₂	¹ S ₁ , ² S ₀	¹ S, ² S
1P ₁ 1R ₁	¹ S ₁ , ² S ₀	¹ S, ² S
1P ₁ 1O ₄	¹ F, ¹ F	¹ F, ¹ F
1P ₁ 1O ₅	¹ G, ¹ G	¹ G
1P ₁ 1Q ₃	² D, ² D	² D, ² D
2 P ₂	¹ P, ¹ D, ¹ S	¹ P

The first clue to the identification of the triplet systems in Pb. III was the detection of the fundamental group ¹D—¹F, which should occur in the visible and quartz regions and which could be examined under different experimental conditions. Observations have also been made in the visible region with a prism spectroscope to find the intense triplet ¹S₁—²P_{0,2}. The result is the identification of the prominent triplet given below :—

TABLE IV.

λ	Int.	ν	Δν
3854.05	12	25939.4	4941
4761.00	6	20998.1	163
4798.27	4	20835.0	

The choice of this is further supported by the detection of the member $1^3D_{33}-2^3P_2$ in the calculated region and by the identification of the triplet 2^3P-2^3S of the sharp secondary series. The 2^3P separation (4941) is found to be in complete agreement with the value predicted from the relativistic doublet law.

The first principal, sharp and diffuse series fall in the extreme ultraviolet which does not lend itself to careful examination of the lines. Attempts were therefore made to fix by extrapolation and then to seek for confirmation by correlating the corresponding members of the spectra of corresponding elements. A very valuable clue to the detection of these members is afforded by the application of the relativity laws to isoelectronic spectra of Hg-like atoms.

An approximate idea of the 1^3P_{12} separation was obtained from the regular doublet sequence and from the relation that in the spectra of the same vertical group of the periodic table ($\frac{\Delta\nu}{Z^2}$) is approximately constant. These give for 1^3P_{12} a value of about 14000 and for 2^3P_{12} , a value between 4000 and 5000.

The following table shows the regular doublet sequence for 1^3P_{12} and 2^3P_{12} separations and the value of ($\frac{\Delta\nu}{Z^2}$) for elements of the same vertical group —

TABLE V —REGULAR DOUBLET SEQUENCE

	1^3P_{12} separation	$\sqrt{\Delta\nu}$	2^3P_{12} separation	$\sqrt{\Delta\nu}$
Hg I	4630.6	8.25	1545.6	6.27
Tl II	9339	9.83	2839	7.30
Pb III	14595	10.99	(4941)	8.40

TABLE VI —VARIATION OF $\Delta\nu/Z^2$

At No Z	Element	2^3P_{12}	$\Delta\nu/Z^2$	1^3P_{12}	$\Delta\nu/Z^2$
6	C III	12.8	356		
14	Si III	73.16	373	263	1.342
32	Ge III	459	448	1642	1.603
50	Sn III	1222.8	491	4031	1.613
82	Pb III	(4941)	60	14595	2.171

The application of the irregular doublet law to Hg like atoms indicated that the probable position of $1^3P_2-1^3S_1$ is at ν 70000 nearly. In applying this sequence the method of Millikan and Bowen is adopted as shown below. In the usual notation, the irregular doublet law may be written as follows —

$$\frac{\nu^2}{R} = \frac{(n_2^2 - n_1^2) Z^2 - Z(n_2^2 \sigma_1 - n_1^2 \sigma_2) + (n_2^2 \sigma^2 - n_1^2 \sigma_2^2)}{n_1^2 n_2^2}$$

When a line results from transition between orbits of two different total quantum numbers, (n_2 & n_1) we get from the above equation, by transposition

$$\nu^2 = \nu - \frac{R(Z-A)^2(n_2^2 - n_1^2)}{n_1^2 n_2^2} = C^2 Z + D^2$$

The expression on the left varies therefore linearly with the atomic number Z, for any given set of values n_2 & n_1 . In the case of $1^3P_2-1^3S_1$ of Hg like atoms $n_1=6$, $n_2=7$ and $A=79$. The progressive variation of with atomic numbers is shown in the following table —

TABLE VII

At No, Z	Element	ν ($1^3P_2-\nu^3S_1$)	$\nu^2 = \nu - 8083(Z-A)^2$	Difference
80	Hg, I	20782	19974	
81	Tl II	43501	40268	20294
82	Pb III	(71093)	63818	22550

Attempts have also been made, by the application of the Mosley law to the spectra of Ge III & Sn III and to the spectra of Hg-like atoms, to fix the approximate position of this triplet as a check on the irregular

doublet sequence. A careful search was then made for the possible triplet $1^3P_{012}-1^3S_1$ among Carroll's ¹⁸ measures, below 1450 Å, having in view the relative order and magnitude of intensities and the probable ratio of intervals between the lines, with the result that the following triplet was fixed.

TABLE VIII.

λ	Int.	ν	Combination.	
1406.6	2	71093	$1^3P_2-1^3S_1$	14595
1167.0	4	85690	$1^3P_1-1^3S_1$	3994
1115.0	2	89686	$1^3P_0-1^3S_1$	

Evidence for the possibility of this being the triplet in question is sought by searching for the complete six-line multiplet (diffuse) 1^3P-1^3D .

The triplet $2^3P_2-2^3S_1$ being fixed in the case of Pb III, attempts have been made by the application of the irregular doublet sequence to locate the corresponding triplet in the case of Tl II, which has not been identified. In this case $n_2 = 8$, $n_1 = 7$ and $A = 79$.

$$\frac{R(n_2^2 - n_1^2)}{n_1^2 n_2^2} = 584.61.$$

The sequence is—

Z	Element.	ν .	$\nu^2 = \nu - 524.6 (Z-A)^2$.
80	Hg. I	2753.6	2229.0
81	Tl. II	...	[9690]
82	Pb. III	21868.8	17146.9

The interpolated value of ν^2 for Tl II is $\nu^2 = 9690 (\pm 500)$.

$\therefore \nu = 9690 + 2097 (\pm 500) = 11787 (\pm 500)$, which is in the infra red, at about 8500-Å.

A very interesting feature noticed in the spark spectrum of Lead is the partial inversion of the triplet F term, 1^3F_3 being negative. The location and identification of the complete six-line multiplet 1^3F-1^3G , in approximately the calculated position is a strong evidence as to the correctness of the identification of the ³F terms.

The singlet system of lines is generally the most difficult to work out. When this analysis was first undertaken not much progress could be made at first in the identification of the singlet spectrum. The strong line 1048.9 (12) was suggested as $1^1S_0-1^1P_1$ and 1553.1 (20) as $1^1S_0-1^1P_1$. While this work was in progress, the author's attention was drawn to a similar publication by Smith ¹⁴. Although there is good agreement between the results of Smith and those of the author, there is disagreement in one or two important points. Smith has the following as 1^3P-1^3S and 1^3P-1^3P .

TABLE IX.

	1^3P_2 .	1^3P_1 .	1^3P_0 .
3S_1	76447 (15)	91047 (10)	95036 (7)
3P_0	...	78157 (15)	
P_1	71095 (12)	85694 (15)	89687
\bar{P}_2	85833 (15)	100428 (10)	

It was pointed out in a note communicated to Nature ¹⁵ that evidently Smith had the author's 1^3S_1 as his 1^3P_1 and that 1^3S_1 suggested by the writer was further supported by the location and identification of the second series 1^3S-2^3P , 1^3D-2^3P & 2^3P-2^3S . The 1^3P-1^3S suggested by the author followed the irregular doublet law for the isoelectronic spectra of Hg-like atoms more closely. The author therefore suggested that an interchange of the two levels 1^3S_1 & $1^3\bar{P}_1$ of Smith would bring the whole scheme into alignment. Attempts have also been made by the writer to identify the singlet spectrum, the results of which

have been published in a paper Smith¹⁴ has since published another paper on the second spark spectrum of lead, in which the suggested modification was adopted. There are still however two main points of disagreement between the classification of the writer and that of Smith. The term $\nu = 101434$, classified by the author as $6s\ 6d\ ^1D_2$, is classified by Smith as $6s\ 7s\ ^1S_0$. Smith classified 1768 67 (56540) as $1\ ^1P_1 - 1\ ^1D_2$, while the writer classified 1711 1 (58442) as this combination. It will be seen from the irregular doublet sequence shown below (Table X), that both $1\ ^1P_1 - 1\ ^1D_2$ and $1\ ^1D_2 - 2\ ^1P_1$ identified by the writer show a distinctly better progression than those of Smith. Further the line $1\ ^1P_1 - 1\ ^1D_2$ should be a strong line. It is found that most of these strong lines of the triplet and singlet systems are found in the wavelength measures of McLennan, Young and Ireton, Bloch and Lang. But the line 1768 67 identified by Smith as $1\ ^1P_1 - 1\ ^1D_2$ is not recorded by any of the previous investigators, while Carrol includes it as one of the lines belonging to Al. These considerations indicate that the writer's classification and identification of $1\ ^1D_2$ is more probable.

TABLE X—IRREGULAR DOUBLET SEQUENCE

	$1\ ^1S_0 - 1\ ^3P_1$	$1\ ^1S_0 - 1\ ^1P_1$	$1\ ^1P_1 - 1\ ^1D_2$
Hg I	39413	54065	17265
Tl II	52390	75656	39501
Pb III	64387	95338	58442 - 56540

From the beginning of this investigation of the analysis of Pb III, it was felt that $^3P\ ^3P$ group should be strong as in the case of the chemically analogous atoms or ions. $1\ ^1D_2$ and $2\ ^1D_2$ terms of Smith are probably $1\ ^3\bar{P}_1$ and $2\ ^3\bar{P}_1$. On this supposition $^3P\ ^3\bar{P}$ group and the resulting combinations have been identified by the author, thus supporting the validity of the writer's identification of $1\ ^1D_2$ term. The term values have been determined by assuming $1\ ^3F_4 = 64\ 800$, ($\frac{\nu}{9} = 7200$). The resonance and ionisation potentials are 7.95 and 31.5 volts respectively, the largest term $1\ ^1S_0 = 255216$. The details of the triplet and singlet systems identified in this investigation are given in the accompanying tables. Table XV gives the configurations and term values for Tl II and Pb III and Table XVI gives other unclassified members of $^3P_{1,2}$ differences.

TABLE XI

	$1\ ^3P_2$ 176234	(14595)	$1\ ^3P_1$ 190829	(8994)	$1\ ^3P_0$ 194823
$1\ ^3S_1$ 105141	1406.6 (2)		1167.0 (4)		1115.0 (2)
	71093		85690		89686
$1\ ^3D_1$	1274.6 (0)		1074.7 (3)		1030.5 (3)
	78456		93049		97040
$1\ ^3D_2$	1266.9 (1)		1069.2 (4)		
	78933		93528		
$1\ ^3D_3$	1250.6 (4)				
	79962				
$1\ ^3\bar{P}_0$ 109690			1231.3 (1)		
			81215		
$1\ ^3\bar{P}_1$ 100332	1371.8 (3)		1142.9 (1)		
	72897		87497		(91491)
$1\ ^3\bar{P}_2$ 90207	1165.1 (4)		995.8 (2)		
	85830		100422		

TABLE XII.

	2^3P_3	4941	2^3P_1	164	2^3P_0
	79202		84143		84307
1^3S_1	3854'11		4761'0		4798'27
105141	25939 (10s)		20998 (8s)		20835 (6s)
2^3S_1	4571'45		3729'06		3706'22
57334	21868'8 (7s)		26808'8 (4)		26974 (3)
1^3D_3	5857'59 (6)				
96272	17067'1 obs. 17070 cal.				
1^3D_2	5523'5 (5)				
97304	18099'4 obs. 18102'0 cal.		Inf. red.		
1^3D_1			Inf. red.		Inf. red.
97785					
1^3P_2	Inf. red.		Inf. red.		
90407					
1^3P_1	4141'56		5207'17		5252'33
103332	24139 (3)		19199 (6)		19034 (3)
1^3P_0			(25570)		3952'1
109690					25296 (8)
2^3D_1	3939'77		3297'64		3279'91
53827	25375'0		30316 (4)		304799 (2)
2^3D_2	3907'17		3276'19		
53628	25573'7 (5)		30514'5 (7)		
2^3D_3	3841'6				
53179	26023'3 (7)				

TABLE XIII.

	1^3F_4	(643)	1^3F_3	(-502)	1^3F_2
	64800		65443		64941
1^3D_3	3176'59		3242'95		3191'49
96272	31471'2 (10)		30827'3 (9)		31324'3 (1)
1^3D_2			3137'87		3089'17
97304			31859 (10)		32361'8 (7)
1^3D_1					3043'9
97785					32843'1 (10)
1^3G_5	3505'37				
36280	28519'5 (3)				
1^3G_4	3563'06		3483'46		
36742	28057'8 (4)		28698'9 (9)		
1^3G_3	3674'75		3589'81		3655'56
37595	27205 (4)		27848'7 (7)		27347'8 (8)

TABLE XIV.—SINGLET SYSTEMS.

Classification.	λ	Int.	Observed. ν	Calculated. ν
$1^1S_0-1^3P_1$	1553'1	20	64387	...
$1^1S_0-1^1P_1$	1048'9	12	95338	...
$1^1P_1-1^3S_1$	1826'2	0	54759	54737
$1^1P_1-1^3D_2$	1597'8	0	62586	62577
$1^1P_1-1^3D_1$	1610'1	1	62107	62103
$1^3S_1-2^3P_1$	3689'22	7	27098'2	...
$2^3P_1-2^3S_1$	4827'1	1	20710'4	20709
$2^3P_1-2^3D_2$	3827'66	8	26118'2	...
$1^3P_1-1^1D_2$	1118'6	3	89397	89393
$1^1P_1-1^1D_2$	1711'1	4	58442	...
$1^1D_2-2^1P_1$	4272'64	8	23398	23393
$1^1D_2-2^3P_2$	4496'12	3	22235	22234
$1^1D_2-2^3P_1$	5779'75	4	17297	17294
$1^3D_1-2^3P_1$	5192'29	4	19254	19260
$1^3D_2-2^3P_1$	5062'90	3	19746	19741
$1^1D_2-1^1F_3$	3560'75	6	28076	...
$1^3D_2-1^1F_3$	4174'38	4	23949	...
$2^3P_1-\alpha$	3832'94	10	26082	...
$2^3P_1-\alpha$	5003'59	3	19980	...
$1^1D_2-\beta$	4182'84	8	23903	...
$1^1D_2-\beta$	3567'16	3	28026	...

The term α above is probably 2^1D_2 term, while β is of the nature of an F term and is probably a 1^1F_3 .

TABLE XV.—CONFIGURATIONS AND TERM VALUES FOR Tl. II & Pb. III.

Electron configuration.	Term.	Term values for Tl. II.	Term values for Pb. III.
$2 P_1$	1^1S_0	164227	255216
$1P_11P_2$	1^3P_2	102499	176234
	3^3P_1	111837	190829
	3^3P_0	114784	194823
	1^1P_1	88565	159879
$1P_11P_3$	1^3D_1	47403	96272
	3^1D_2	47797	97304
	3^1D_1	48082	97785
	1^1D_2	49064	101434
$1P_11Q_1$	1^3S_1	59008	105141
$1P_11R_1$	2^3S_1	...	57334
$1P_11Q_2$	2^3P_2	42199	79202
	3^3P_1	44650	84143
	3^3P_0	44866	84307
	2^3P_1	38020	78043
$1P_11Q_3$	2^3D_2	26023	53179
	3^1D_2	26172	53628
	3^1D_1	26300	53827
	2^3D_2	27333	58063
$1P_11P_4$	1^3F_4	(28000)	(64800)
	3^1F_3	28114	65443
	3^1F_2	28014	64941
	1^3F_3	...	73358
$1P_11P_5$	1^3G_2	...	36280
	3^1G_4	...	36742
	3^1G_3	...	37595

TABLE XVI.—OTHER UNCLASSIFIED MEMBERS OF Pb. III.

	1^3P_2	1^3P_1	1^3P_0
1.	1165.1 (10) 76447	995.8 (2) 91047	
2.	1073.1 (1) 93188	927.7 (3) 107794	894.4 (4) 111807
3.	1028.7 (10) 97210	894.4 (4) 111807	
4.	908.5 (0) 110072	802.07 124677	
5.	888.5 (3) 112549	786.48 (1) 127149	
6.	860.6 (0) 116200	764.57 (2) 130792	
7.	840.99 (5) 118908	749.09 (3) 133495	
8.	802.03 (5) 124684	718.07 (2) 139262	

Triplet number 7 is identified by Smith, recently as 1^3P-2^3S ; but the line 137491 classified by him as $1^5P_0-2^3S_1$ is not recorded either by Carroll or Mack.

Spectrum of Pb. IV.

The first successful attempt to find series regularities among the wavelengths of trebly-ionised spectrum of lead, was that made by Carroll⁸, who identified the first members of the principal and diffuse series occurring in the vacuum grating region. In a recent communication¹⁰, the present writer set forth the leading members of the secondary series, which may be expected in the region of longer wavelengths.

The term structure of the spectrum of Pb. IV is generally similar in character to that of any chemically analogous atom or ion. Of these the spectra of Au I, Hg II and Tl. III and those of Ge IV and Sn IV have already been analysed to some extent. We have in the atom of Pb. IV, a one electron system, which normally gives the simplest type of alkali-like doublet spectrum. As the electron runs successively through $P_1, P_2, P_3, Q_1, \dots$ shells, the terms $1^2S, 1^2P, 1^2D, 2^2S$, etc., are obtained, the largest term being 1^2S_1 . The more complicated scheme of doublets and quartets result, when one or more of the inner group of 10 O_3 electrons is excited. The terms which different electron configurations give rise to may be calculated according to the principles developed by Pauli, Heisenberg & Hund and are given in the following table. It will be seen from the table that corresponding to the addition of an electron to the three different states ($1^2S, 1^2D, 1^2D$) of the Pb V core, three distinct families of terms arise.

TABLE XVII.

K L M N $1_1, \dots, 4_4$	O					P			Term prefix.	Terms predicted.	Series limit Pb V term.	
	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3				
60	2	6	10			(1)			$6s$	} 1^2S		
60	2	6	10				(1)		$6p$			
60	2	6	10					(1)	$6d$			
60	2	6	9			1(1)			$6s^2$			3^2D
60	2	6	9			1	(1)		$6p^2$			3^2D
60	2	6	9			1		(1)	$6d^2$		3^2D	
											1^2D	

The analysis of Cu I Zn II Au I & Hg II has shown that in addition to the regular doublet systems built on the d^0 ion there is another important family of terms built on the d^9s ion characterized by doublet and quartet terms. The deepest term of this system is a metastable D term which is inverted and very low. The separation of this deep lying D (d^9s) term can be found approximately by the relativistic doublet formula and by a knowledge of the D (d^9s) difference of the next higher ion. As both these sources of information were available attempts were made to identify this inverted D term. Further in Cu I Zn II Au I etc. The metastable D term is found to combine strongly with the regular P term (d^9p) and with the quartet terms arising from the d^9sp configuration. The recent analysis of the second spark spectrum of Thallium by the author has shown that these terms are found in the spectrum of Tl III⁴⁷. After the publication of the above mentioned report by the writer Smith published a preliminary report of a similar investigation where he suggests an alternative classification which without adducing any reasons he mentions as more probable. From the application of the relativistic doublet law to isoelectronic spectra (Au I Hg II Tl III and Pb IV) and from a study of the progressive variation ΔZ in the homologous spectra C IV S IV Ge IV & Sn IV it was thought from the beginning of this investigation that ($2^3P_2-2^3P_1$) should be of the order of 7000 ± 600 . With the aid of the information available to the author regarding the stages of ionisation of the spectral lines in the visible and quartz regions a search was made for the frequency recurrence among the Pb IV lines and it was found that there were three alternative schemes as constituting the probable doublet systems with ($2^3P_2-2^3P_1$) = 6838 7131 8063 respectively. It is the pairs of the wavelengths with the last mentioned frequency difference that were given by Smith as the more probable. Relativity doublet sequence and progression of $\frac{\Delta}{Z}$ for the doublet separations are given in Tables XXI and XX. The doublet systems classified by the writer are given in Table XXI.

TABLE XVIII—PAIRS WITH FREQUENCY DIFFERENCES

<u>6838</u>	<u>7131</u>	<u>8063</u>
24139	23903	24680
30979	31037	32749
26730	25573	25229
33567	32704	33294
32362	34032	31780
39200	41162	39847
33007	36325	32548
39847	43458	40613

TABLE XIX—REGULAR DOUBLET SEQUENCE

	1^3P_2	$^4\Delta$	$2^3P_2\Delta$	$^4\Delta$
Au I	3815	7859		
Hg II	91227	9773	3672	776
Tl III	14811	11031	5682	860
Pb IV	21060	12047	7130	917

TABLE XX—VARIATION OF DOUBLET SEPARATION WITH Z

At. N	Z	Element	$2P-2P$	Δ/Z^2	$1P-1P$	Δ/Z
6		C IV			1074	2983
14		Si IV	162	826	4600	2347
32		Ge IV	942	92	2790	2726
50		Sn IV	2177.4	871	6507	2602
82		Pb IV	7130	10	21060	3130

TABLE XXI.—DOUBLET SYSTEMS OF Pb. IV.

	λ		ν	
$1^2S_1-1^2P_1$	1313.2 (9)		76150	} 21060
-1^2P_2	1028.7 (10)		97210	
$1^2P_2-1^2D_2$	1145.0 (3)		87336	} 21065
-1^2D_3	1116.2 (4)		89590	
$1^2P_1-1^2D_2$	922.5 (4)		108401	
$1P-2^2S$	1123.45 (3)		89012	} 21055
$1^2P_1-2^2S_1$	908.54 (5)		110067	
$2^2S_1-2^2P_1$	4182.40 (8s)		23903	} 7133
-2^2P_2	3221.00 (10)		31037	
$1^2D_2-2^2P_1$	3909.29 (5d)		25573	} 7131
$^2D_3-P_2$	3280.09 (9)		30478	
$^2D_2-P_2$	3056.84 (4)		32704	
$2^2P-2^2D_2$	2937.55 (4)		34032	} 868
$--D_3$	2864.45 (10)		34900	
$2^2P_1-D_2$	2428.70 (8bd)		41162	
$2^2P_2-3^2S_1$	2752.15 (1)		36325	} 7133
$P_1-3^2S_1$	2300.35 (4s)		43458	
$2^2D_2-2^2F_3$	3483.46 (9)		28699	} 875
D_3-F_3	3592.95 (6s)		27824	

In the first place it should be mentioned that 8,063 given by Smith as 2^2P_2 is found to be abnormally high from the relativistic doublet sequence and from the progressive variation of $\Delta\nu/Z^2$ in the homologous spectra, as shown in the preceding tables. Further, justification for the difference 7130, reported by the author is afforded by the location and identification of the following triplet as $6s^1 2^2D-7p^2P$.

TABLE XXII.

$d^{10}p/d^9s^2$	2D_3	21019	2D_2
2P_1	...		804.55 (1)
(7130)	...		124293
2P_2	655.82 (3)		760.90 (0)
	152439		131420

There is no evidence of a similar combination with either of the remaining two separations. That the difference 21019 cm^{-1} represents the difference $^2D_3-^2D_2$ (d^9s^2) of Pb. IV seems to be confirmed by the following comparison with $^2D_{1/2}$ (d^9s) of the next higher ion.

TABLE XXIII.

Cu.	Ag.	Zn.	Cd.	Tl.	Pb.	
2070	4574	2754	5764	18865	21300(?)	d^9s
2043	4472	2719	5635	18618	21019	d^9s^2

The combinations of this deep lying inverted D term with the quartet terms of the group (d^3sp) are given in the following table —

TABLE XXIV

6p /6	D	D
4F		1407 8 (1)
		71033
F	1749 9 (1)	1279 5 (3)
	57146	78167
F	1439 2 (2)	1104 8 (od)
	69478	90510
D		1308 2 (2)
		76441
D	1437 1 (1d)	1103 6 (od)
	69585	90613
D	1233 6 (3)	979 47 (2)
	81068	102096
D	1096 5 (1d)	
	91189	
4P	1362 60 (0)	1059 3 (1)
	73381	94400
P	1087 34 (2)	884 98 (6)
	91968	112997
P		

Summary and conclusions

The spark spectrum of Lead has been photographed from $\lambda 7000$ to $\lambda 2000$ by using powerful excitation, with a quartz spectrograph and a 10 feet concave grating using iron arc as the standard. Many new lines have been measured mostly produced by the higher stages of ionisation. The wave numbers, wavelengths, intensities together with the stages of ionisation of the prominent ones have been tabulated.

A critical differentiation of the lines belonging respectively to Pb I, Pb II, Pb III, Pb IV resulted from a careful scrutiny of the spectra obtained under varying degrees of excitation.

The analysis of the second and third spark spectra of the element has been discussed in relation to the theoretical expectations and with the accurate and extensive data at hand it has been shown that the spectral structures of Pb III and Pb IV are in all details in complete agreement with Hund's correlation of spectral terms with electron configurations.

The present analysis illustrates in a very convincing manner the utility of the study of the spectra of an element under varying degrees of discharge.

In conclusion I wish to express my gratitude to Dr. T. Royds, the Director of the Kodaikanal Observatory and to Dr. A. L. Narayan, the Assistant Director for their active interest and much helpful criticism throughout the progress of the work. My thanks are also due to the Syndicate of the Madras University for the award of a studentship which has made this work possible.

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Explanation of plates.

I and II Spark Spectra of Lead, Concave Grating Spectrograph.

III and IV Spark Spectra of Lead, Quartz Spectrograph, with increasing inductance a, b, c, d.

KODAIKANAL,
22nd December 1930.

A. S. RAO,
Research Scholar.

PLATE I.
Pb (conc. grating.)

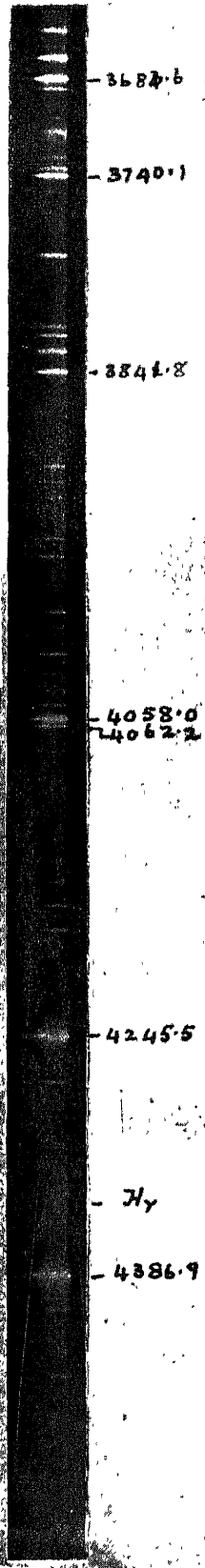


PLATE II.
(Pb. conc. grating.)

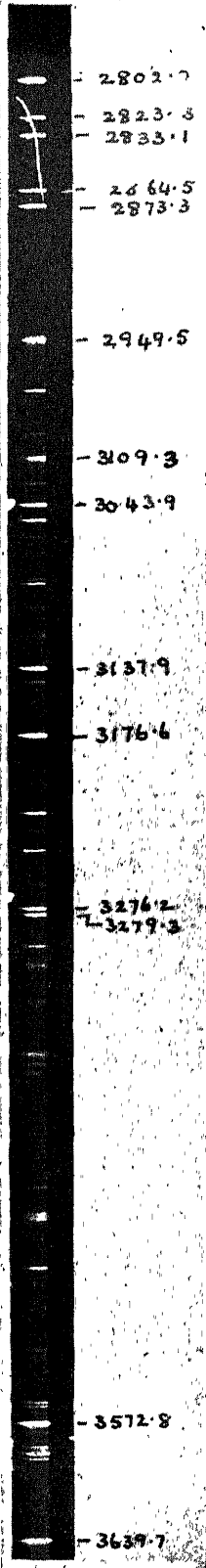


PLATE III.
(Pb. quartz.)

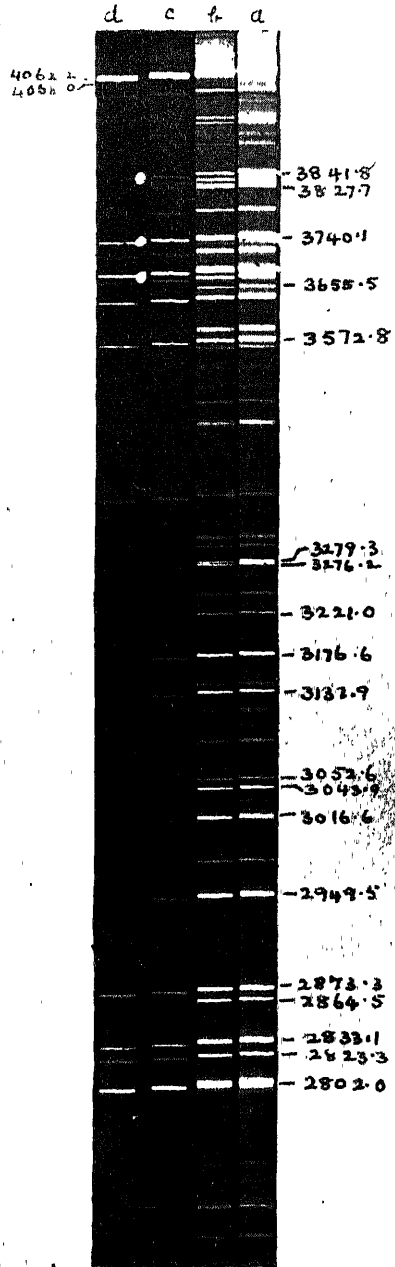


PLATE IV.
(Pb. quartz—cont.)

