THE SECOND SPARK SPECTRUM OF LEAD Pb III

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Abstract

Some additional multiplets arising from combinations between triplet terms of Pb III have been found. These are $6^3P_{0,1,2}-8^3S_1$, $6^3P_{0,1,2}-7^3D_{1,2,3}$, $7^3P_{0,1,2}-7^3D_{1,2,3}$ and $6^3P_{0,1,2}-pp^3P_1$. Twenty-one lines arising from combinations between singlet terms and intercombinations between singlet and triplet terms have been identified. Of particular interest is the pp^1D_2 term which is found in combination with $6^3P_{1,2}$, 6^1P_1, $6^3F_{2,3}$ and 6^1F_3. Seven newly found lines of Tl II are also given, which correspond to some of the Pb III combinations classified in this paper.

The spectrum of Pb III, being similar to that of Hg I and of Tl II, is derived from triplet and singlet terms. The most important terms to be expected are listed in Table I. In the first column the states, with the total quantum numbers, of the two valence electrons, are given, and the second column contains the resultant terms expressed in a notation which is used throughout this paper.

Table I.

State of Electrons	Terms		State of Electrons	Terms		
6s6s		6^1S_0	6p6p	$pp^3P_{0,1,2}$	pp^1D_2	pp^1S_0
6s6p	$6^3P_{0,1,2}$	6^1P_1	6s7s	7^3S_1	7^1S_0	
6s6d	$6^3D_{1,2,3}$	6^1D_2	6s7p	$7^3P_{0,1,2}$	7^1P_1	
6s5f	$5^3F_{2,3,4}$	5^1F_3	6s7d	$7^3D_{1,2,3}$	7^1D_2	

Experimental

Spectrograms have been taken of the spark spectrum of lead in hydrogen at a pressure of about 50 cm of mercury with an auxiliary spark gap in air in series with the main spark. By increasing the length of the auxiliary spark gap the lines belonging to the higher stages of ionization are progressively enhanced. The spark gap was arranged to be parallel to the slit of a Hilger one meter interchangeable spectrograph, employing both glass and quartz trains, so that the condensing lens of the spectrograph projected on to the slit images of the tips of the electrodes. The enhanced lines appear first at the electrode tips and gradually extend across the gap as the excitation voltage is increased by lengthening the auxiliary spark gap. Self induction was also inserted in the circuit and increased until only the arc lines appeared. Spectrograms were also obtained using as source the interrupted arc in air. Alternating voltages up to 1500 volts were applied to the electrodes, which were shunted by a condenser of capacity about 2 microfarads. On increasing the applied voltage, the lines arising from the higher states of ionization of the lead atom appear or become stronger relative to those belonging to lower states. By these methods the lines could be sorted out into groups belonging to the various stages of ionization. Other data used in this investigation were wave-length measures of the vacuum spark spectrum of lead for the Schumann region made by Dr. R. J. Lang by means of a two meter grating, and measures[1] in the region above 2200 made by the writer with a two meter grating on a Rowland mounting.

Combinations of Triplet Terms

A preliminary account[2] of some of the triplet term multiplets has been given by the writer. On referring to a previously published paper[3] by K. R. Rao, A. L. Narayan, and A. S. Rao, which the writer has only recently been able to procure, it was found that the results in the two papers are in agreement for the $6^3P_{0,1,2}$—$6^3D_{1,2,3}$ and $6^3D_{1,2,3}$—$6^3F_{2,3,4}$ groups but differ for the $6^3P_{0,1,2}$—7^3S_1 triplet. In spite of the abnormal intensity relations between the lines chosen by Rao for this triplet—the intensities are given as 2, 4, 2 by Carroll and appear on Lang's plates as 9, 15, 12—it is quite certain that Rao's identification is the correct one. The writer has now found the $6^3P_{0,1,2}$—8^3S_1, $6^3P_{0,1,2}$—$7^3D_{1,2,3}$ and $7^3P_{1,2,3}$—$7^3D_{1,2,3}$ groups which afford ample evidence for the validity of the scheme of triplet term combinations. This scheme is given in Table II. For the sake of completeness the lines previously identified are included. There is still some uncertainty with regard to the $6^3P_{0,1,2}$—$pp^3P_{0,1,2}$ combinations. It seems, however, probable that λλ 1052, 1098 and 1308 constitute the $6^3P_{0,1,2}$—pp^3P_1 triplet, as this assignment would make the wave numbers of 6^3P_1—pp^3P_1 for Hg I, Tl II[4] and Pb III follow very closely the irregular doublet law (See Table V). It might be pointed out that λλ3909, 5857 have been classified as belonging to Pb II by Gieseler.[5]

Singlet Combinations and Intercombinations between Singlet and Triplet terms

On turning to the singlet term combinations the evidence for the validity of the choices made is not so conclusive. A distinctive feature of the spectra of Hg I and Tl II [4,6] is the appearance of strong lines due to intercombinations between singlet and triplet terms. The separations between the various triplet terms already found may therefore be expected to furnish some clue which will be of assistance in identifying these lines. Using the irregular doublet law and extrapolating from the known $6^1S_0-6^1P_1$ and $6^1S_0-6^3P_1$ combinations of Hg I and Tl II the lines λλ 1048, 1553, which are strong in the vacuum spark of lead, are suggested as the corresponding lines for Pb III.

[1] S. Smith, Trans. Roy. Soc. Canada **22**, 331 (1928).
[2] S. Smith, Proc. Nat. Acad. Sci. **14**, 878 (1928).
[3] K. R. Rao, A. L. Narayan, A. S. Rao, Indian Jour. Phys. **2**, 467 (1928).
[4] S. Smith, Proc. Nat. Acad. Sci. **14**, 951 (1928).
[5] Gieseler, Zeits. f. Physik **42**, 276 (1927).
[6] J. C. McLennan, A. B. McLay and M. F. Crawford, Trans. Roy. Soc. Canada **22**, 241 (1928).

Table II. *Triplet term combinations of Pb III.*

	6^3P_0			6^3P_1			6^3P_2	
	†1030.44	(15)		†1074.63	(15)		†1274.56	(10)
6^3D_1	97046		3991	93055		14597	78458	
				477			482	
				†1069.15	(20)		†1266.79	(15)
6^3D_2				93532		14592	78940	
							1032	
							†1250.43	(20)
6^3D_3							79972	
	*1114.99	(9)		*1166.94	(15)		*1406.57	(12)
7^3S_1	89687		3993	85694		14599	71095	
	727.32	(0)		749.08	(3)		840.97	(4)
8^3S_1	137491		3994	133497		14587	118910	
	709.24	(3)		729.91	(0)		816.97	(0)
7^3D_1	140996		3993	137003		14599	122404	
				198			220	
				728.86	(4)		815.50	(2)
7^3D_2				137201		14577	122624	
							444	
							812.56	(5)
7^3D_3							123068	
	1052.23	(7)		1098.39	(10)		1308.10	(15)
pp^3P_1	95036		3994	91042		14595	76447	
	7^3P_0			7^3P_1			7^3P_2	
	*4798.52	(4)		*4761.03	(8)		*3854.04	(10)
7^3S_1	20834.0		164.0	20998.0		4941.5	25939.5	
	*3706.13	(2)		*3728.83	(3)		*4571.35	(5)
8^3S_1	26974.7		164.2	26810.5		4941.2	21869.3	
	3279.91	(2)		3297.64	(4)		3939.77	(1)
7^3D_1	30479.9		163.9	30316.0		4941.0	25375.0	
				198.5			198.7	
				3276.19	(7)		3909.17	(5)
7^3D_2				30514.5		4940.8	25573.7	
							449.6	
							3841.62	(7)
7^3D_3							26023.3	
	6^3D_1			6^3D_2			6^3D_3	
				†3137.92	(10)		†3242.86	(5)
5^3F_3				31859.0		1030.9	30828.1	
				502.9			502.1	
	†3043.92	(10)		†3089.16	(6)		3190.89	(0)
5^3F_2	32842.8		480.9	32361.9		1031.7	31330.2	
							140.8	
							†3176.61	(10)
5^3F_4							31471.0	
				*5523.5	(5)		*5857.67	(6)
7^3P_2				18099.7		1032.2	17067.5	

† Lines identified by Rao, Narayan, Rao and Smith.
* Lines identified by Rao, Narayan and Rao.

These lead to a wave-number difference of 30953 for $6^3P_1-6^1P_1$. Predictions can now be made for the $6^1P_1-6^3D_{1,2}$ and $6^1P_1-7^3S_1$ combinations. Lines are found to appear very close to the predicted postitons, as is shown in Table III. If λλ 1142, 1371, which have the appropriate separation, are selected as $6^3P_{1,2}-6^1D_2$ then λ1768 would be $6^1P_1-6^1D_2$. The wave-number

TABLE III. *Singlet term combinations and intercombinations with triplet terms.*

Combination	λ	Int.	ν Observed	ν Predicted
$6^1S_0-6^1P_1$	1048.86	50	95341	
$6^1S_0-6^3P_1$	1553.09	10	64388	
$6^1P_1-6^3D_1$	1610.34	2	62099	62102
$6^1P_1-6^3D_2$	1597.96	2	62580	62579
$6^3P_1-6^1D_2$	1142.93	5	87494	
$6^3P_2-6^1D_2$	1371.80	6	72897	72899
$6^1P_1-6^1D_2$	1768.67	6	56540	56541
$6^1P_1-7^3S_1$	1826.86	2	54739	54741
$6^1D_2-5^3F_3$	2637.70	1	37900.5	37899
$6^1D_2-5^1F_3$	2562.27	10	39016.2	
$6^3D_2-5^1F_3$	3031.65	4	32975.8	32976
$6^3D_3-5^1F_3$	3129.63	0	31943.4	31944
$6^1D_2-7^3P_2$	4141.42	3	24139.5	24138
$6^1D_2-7^3P_1$	5207.15	3	19199.0	19197
$6^3P_1-pp^1D_2$	995.75	10	100427	
$6^1P_1-pp^1D_2$	1439.42	15	69472	69474
$6^3P_2-pp^1D_2$	1165.05	8	85833	85832
$pp^1D_2-5^1F_3$	3832.83	6	26083.0	26083
$pp^1D_2-5^3F_3$	4004.16	2	24967.0	24965
$pp^1D_2-5^3F_2$	3925.23	0	25469.0	25468
$pp^3P_1-5^3F_2$	2868.16	2	34855.4	34852

The wave-lengths below 2000A are in I.A. vac.
Those above 2000A are in I.A. air.

difference 6040 of $6^1D_2-6^3D_2$ can then be applied to predict the position of $6^1D_2-5^3F_3$ which is apparently the line λ2637. The strong line λ2562 appears to be $6^1D_2-5^1F_3$ as the 6040 separation of $6^1D_2-6^3D_2$ and the 1032 separation of $6^3D_2-6^3D_2$ lead to observed lines at λλ3031, 3129.

The group of strong lines λλ995, 1165, 1439 are of particular interest. They may be expressed as 6^3P_1-x, 6^3P_2-x and 6^1P_1-x. The only other terms with which x has been found to combine are 5^3F_2, 5^3F_3 and 5^1F_3. The obvious conclusion is that x is the pp^1D_2 term. According to the rules for the transitions between states of atoms with two valence electrons,[7] the pp^1D_2 term, which arises from a $6p$ $6p$ arrangement, can combine with terms arising from the following states:

(a)	$ns\cdot np$	$\Delta l_1=-1$	$\Delta l_2=0$
(b)	$np\cdot nd$	$\Delta l_1=0$	$\Delta l_2=1$
(c)	$ns\cdot nf$	$\Delta l_1=-1$	$\Delta l_2=2$
(d)	$nd\cdot nf$	$\Delta l_1=1$	$\Delta l_2=2$

Of all the terms which result from these configurations only those arising from (a) and (c) are known. The lowest of these are $6^3P_{0,1,2}$, 6^1P_1, $5^3F_{2,3,4}$ and

[7] W. Grotrian, Graphische Darstellung der Spektren p. 204, Springer, (1928).

5^1F_3. The selection rule for inner quantum numbers limits the terms with which pp^1D_2 can combine to $6^3P_{1,2}$, 6^1P_1, $5^3F_{2,3}$ and 5^1F_3. All these combinations have been found. The combinations $4^3P_{1,2}-pp^1D_2$ for Zn I have been given by Sawyer[8].

Of the classified lines recorded in Table III the identity of five has been assumed and the wave-numbers of the remaining sixteen have been predicted on the basis of these five identifications and of the triplet combination assignments of Table II.

In order to obtain the term values the difference 7^3S_1—8^3S_1 has been used in a Rydberg formula giving the approximate value 109400 for 7^3S_1. In the case of Hg I a similar calculation gives a value for 7^3S_1 which is one and a half percent larger than the true value. Assuming that a corresponding correction should be applied in the case of Pb III, the value of 7^3S_1 may be taken to be 107750. A similar process carried out on the $6^3D_1-7^3D_1$ difference gives a value 102325 for 6^3D_1. This would lead to a value 109700 for 7^3S_1. 108700, which is approximately the mean of these two values of 7^3S_1 has been used to obtain the term values given in Table IV. The ionization potential of the doubly ionized atom of lead is found to be 31.93 volts. The resonance potential is 7.95 volts.

TABLE IV. *Term Values of Pb III.*

Term	Value	Term	Value	Term	Value	Term	Value
6^1S_0	258778	6^1D_2	106896	7^3P_0	87866	5^1F_3	67880
6^3P_0	198383	pp^3P_1	103347	7^3P_1	87702	8^3S_1	60891
6^3P_1	194390	6^3D_1	101337	7^3P_2	82761	7^3D_1	57386
6^3P_2	179795	6^3D_2	100856	5^3F_3	68998	7^3D_2	57187
6^1P_1	163437	6^3D_3	99825	5^3F_2	68495	7^3D_3	56737
7^3S_1	(108700)	pp^1D_2	93963	5^3F_4	68354		

Since both 6^1D_2 and pp^1D_2 combine with the same P and F terms it is possible that the two term values in Table IV for 6^1D_2 and pp^1D_2 should be interchanged. The main argument in favor of the choice given here is that in the case of Mg I, Zn I, Cd I, Hg I and Tl II the $^1D_2$ term in each case is lower than the corresponding $^3D_1$ term. If 89108 were taken as 6^1D_2 then the 6^3D_1 term would be lower than this value by 7375. Also the assigned value of 89108 for pp^1D_2 is in reasonably good agreement with the expected relative values of the pp^3P_1 and pp^1D_2 terms.

The sequence of values of the wave-numbers of $6^3P_1-pp^3P_1$, $6^1S_0-6^1P_1$ and $6^1S_0-6^3P_1$ for mercury-like atoms is given in Table V.

TABLE V. *Irregular doublet law for mercury-like atoms.*

	$6^3P_1-pp^3P_1$	Difference	$6^1S_0-6^1P_1$	Difference	$6^1S_0-6^3P_1$	Difference
Hg I	54576		54066		39412	
		18365		21590		12981
Tl II	72941		75656		52393	
		18101		19685		11995
Pb III	91042		95341		64388	

[8] R. A. Sawyer, J.O.S.A. **13**, 432 (1926).

NOTE ON THE SPECTRUM OF Tl II.

A search has been made in the spectrum of Tl II for the combinations of the pp^1D_2 term with the $6^3P_{1,2}$ and 6^1P_1 terms. These three combinations have been found, and are given in Table VI, together with some combinations additional to those already classified[4,6]. The $ppD5F$ combinations would be expected to lie far in the infra-red, the calculated wave-number of $5^1F_3-pp^1D_2$ being 7447.

TABLE VI. *Some further lines of Tl II.*

Classification	λ	Intensity	ν
$6^3P_1-pp^1D_2$	1308.52	2	76422
$6^3P_2-pp^1D_2$	1490.50	5	67092
$6^1P_1-pp^1D_2$	1881.22	6	53157
$6^1D_2-5^1F_3$	4737.07	30	21104.0
$6^1D_2-5^3F_3$	4770.88	1	20954.6
$6^3D_2-5^1F_3$	5040.69	0	19833.0
$6^3D_3-5^1F_3$	5143.7	0	19436

The line λ5143 is taken from MacQuarrie's wave-length measures[9] of the spectrum obtained from an electrodeless discharge in thallium vapor. λλ4770, 5041 and 5143 are given by MacQuarrie as Tl III lines. It should be mentioned that λ1490 had previously been classified by the writer as $6^3P_1-pp^3P_0$.

THE PRINCIPAL QUANTUM NUMBERS OF THE LOWEST FUNDAMENTAL TERMS

The principal quantum numbers of the lowest S, P, D and F terms of the elements have been assigned on more or less theoretical grounds by Bohr and others. The conclusions arrived at are given in a clear and concise manner by Grotrian.[7] The lowest F terms of the zinc-like system and of the cadmium-like system are stated to have the principal quantum number 4 while 5 is given as the principal quantum number of the lowest F terms of mercury-like system. Combinations between the lowest ^3D terms, and terms which are generally supposed to be the lowest[3] F terms, have been identified for some of the atoms in the above mentioned systems by various investigators.

The wave-numbers of the $^3D_3-{}^3F_4$ members are collected in Table VII. If x is assigned the value 4, as is the usual practice, it is surprising to find that the wave-numbers do not follow the irregular doublet law. The generally accepted value of y is 4 and yet it will be observed that the wave-number differences are almost equal for the cadmium-like sequence, indicating that y should probably be given the value 5. It may be that the lowest ^3F terms for these atoms have yet to be found. In the case of the mercury-like system the wave-number differences suggest that z should be assigned the value 6. However, in the present paper the more generally accepted value 5 has been used.

[9] W. C. MacQuarrie, Trans. Roy. Soc. Canada 19, 57 (1925).

TABLE VII.

	$4^3D_3-x^3F_4$	Difference		$5^3D_3-y^3F_4$	Difference		$6^3D_3-z^3F_4$	Difference
Zn I[10]	6060		Cd I[10]	6066		Hg I[10]	5815	
		17396			15286			13588
Ga II[11]	23456		In II[11,12]	21352		Tl II [3]	19403	
		24045			16251			12068
Ge III[13]	47501		Sn III[12]	37603		Pb III[2,3]	31471	

In conclusion I wish to thank Dr. Lang for the use of his list of wave-lengths in the Schumann region and to acknowledge a grant from the National Research Council of Canada.

Note added July 3, 1929. Since the above paper was written I have been investigating the Schüler lamp discharge of thallium. The lines λλ5040 and 5143 classified above in Table VI as $6^3D_{2,3}-5^1F_3$ appear on the plates with intensities 3 and 1 respectively. The new measures are 5040.50A and 5142.84A and give a wave-number difference fo 4937 for $6^3D_2-6^3D_3$. There can now be no doubt that these lines belong to Tl II and the evidence in support of the classification in Table VI is further strengthened.

[10] A. Fowler, Series in Line Spectra, 1922.
[11] K. R. Rao, Proc. Phys. Soc. London **39**, 161 (1927).
[12] J. B. Green and R. A. Loring, Phys. Rev. **30**, 574 (1927).
[13] R. J. Lang, Proc. Nat. Acad. Sci. **14**, 32 (1928).