THE INFRARED SPECTRUM OF SN I

By H. M. Randall and Norman Wright
University of Michigan
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Abstract

An open arc of 80 amperes between a carbon rod and tin pool has been used as source, and observations have been made using a grating spectrometer and thermopile. The wave-lengths of forty-five new lines of the tin arc spectrum in the region from 1μ to 3μ have been measured, and rough determinations of the relative intensities of the strong lines have been made. Nine energy levels of the $5s^25p6p$ configuration have been found, which with the one found by Green and Loring complete the set. Three of the four levels of the $5s^25p(^2P_{1/2})4f$ set have been found, and the fourth, 3_3, has been accounted for as lying too close to 4_2 for resolution. With the fixing of these levels all the strong infra-red lines have been classified. The finding of the levels $5p(^2P_{1/2})4f4_2$ and $5p(^2P_{1/2})5f4_2$ has made possible a good determination of the absolute term values.

THE tin atom in its lowest state has the electron configuration $5s^25p^2$ which gives rise to five low energy levels. The next higher groups of levels from which transitions can be made to the low levels are those due to the configurations $5s^25p6s$ and $5s^25p5d$. The relative term values of these levels have been well established by the work of McLennan, Young, and McLay,[1] Sponer,[2] and Zumstein.[3] A tentative classification of the levels was made by Sur.[4] Later Back[5] and Green and Loring[6] observing Zeeman effects corrected and practically completed the classification. A study of the spectrum of SnII by Green and Loring[6] showed the separation of the $5s^25p^2P_{\frac{1}{2},1\frac{1}{2}}$ levels to be 4252 cm^{-1}.

Another configuration of the neutral tin atom, $5s^25p6p$, gives rise to ten levels which of course cannot combine with the levels of the normal configuration $5s^25p^2$ but which can combine with the levels of both the $5p6s$ and $5p5d$ configurations. These ten levels should be divided into two groups, a group of four levels with $J=0, 1, 1, 2$ built upon the $5p^2P_{1/2}$ state of SnII, and above these by roughly the SnII^2P separation a group of six levels with $J=0, 1, 1, 2, 2, 3$ built upon the $5p^2P_{1\frac{1}{2}}$ state of SnII. Green and Loring using the infrared lines measured by Randall[7] found only the $5p(^2P_{1/2})6p3_1$ (designated $^3P_1$) level of this set. The purpose of this work was to re-investigate the region of the tin arc spectrum from 0.8μ to 1.3μ observed by Randall and to extend the measurements to 3μ in the hope of finding more of these levels.

[1] J. C. McLennan, J. F. T. Young, and A. B. McLay, Trans. Roy. Soc. Canada Sec. III, 57 (1924).
[2] H. Sponer, Zeits. f. Physik **32,** 19 (1925).
[3] R. V. Zumstein, Phys. Rev. **27,** 150 (1926).
[4] N. K. Sur, Zeits. f. Physik **41,** 791 (1927).
[5] E. Back, Zeits. f. Physik **43,** 309 (1927).
[6] J. B. Green and R. A. Loring, Phys. Rev. **30,** 575 (1927).
[7] H. M. Randall, Astrophys. J. **34,** (1911).

Experimental

The source of radiation was an open air arc, a pool of molten tin in a carbon or iron cup forming the cathode and a carbon stick the anode. The current was taken from a 250 volt d.c. motor-generator and maintained at an average of 80 amperes. The nitrogen, oxygen, and carbon lines which come out strongly at a current of 125 amperes could not be detected at 80 amperes. The only impurity which gave lines of observable intensity was potassium which was present in the carbons.

The spectrometer employed in this work is a grating instrument that has been in use in this laboratory for many years. It was recently described by Ingram[8] in his work on carbon and nitrogen. The thermopile and thermorelay were also described by him. For this work a Michigan grating, of echelette type, ruled by Barker on a nickel surface, gave very good intensity throughout the spectral region covered. It was ruled with 14400 lines per inch. With the slit width used a spectral range of 10A at 1.5μ was transmitted. The smallest separation resolvable was probably about 15A. The method of setting upon lines for measurement was that described by Randall.[7] The error in the measurements is roughly within 2A.

Since the deflection of the galvanometer as any particular line was observed varied greatly depending on the level of the tin in the pool, the gap length, etc., the relative intensities of a number of the stronger lines were obtained in the following manner. The arc would be struck and allowed a few seconds to become steady after which the instrument would be turned in succession over two adjacent lines and back again, the galvanometer deflection in each case being noted. The arc would then be shut off, the whole process having required about one minute. Then one of these lines and its other neighbor would be selected and the process repeated. The ratios of the deflections for adjacent lines were then computed. Taking a deflection of 2000 mm as average for the line λ11457A, the corresponding deflections for the other lines were found using these ratios. The deflections calculated in this manner are in italics in Table I. For adjacent lines the ratio of the intensities as given should not be in error by more than 15 percent. The intensities not in italics in the table are merely rough averages of the galvanometer deflections taken at different times.

Sn I Wave-lengths and Assignments

Table I is a list of the newly measured infrared wave-lengths together with the previous measurements of Randall. Some photographic lines measured by Walters[9] which have been classified in this work are added at the end of the table. Table II gives the classified levels of Sn I. Levels found in this work are marked by asterisks.

The levels sought, i.e. those of the $5p6p$ configuration, were all found. The positions of two of these levels, $5p6p6_3$ and $5p6p9_0$, were based on but one combination each; the justification of this will be seen in what follows. The

[8] S. B. Ingram, Phys. Rev. **34**, 421 (1929).

[9] F. M. Walters, Bur. Stand. J. 411 (1921).

TABLE I.

Wave-lengths (I. A.)	Wave-numbers (vacuum)	Int.	$\nu_{calc}-\nu_{obs}$	Assignments
24740.0	4041.0	40		
24329.0	4109.2	40	0.5	$6s^1P_1^0-6p3_1$
22999.0	4346.8	30		
22133.5	4516.8	40	1.9	$6p10_1-7s^1P_1^0$
21688.0	4609.6	80	1.4	$6p8_2-7s^3P_2^0$
20863.5	4791.8	400	1.2	$6p4_2-7s8_1^0$
20624.0	4847.4	200	1.6	$6p3_1-7s7_0^0$
20596.2	4854.0	70	1.8	$6p3_1-7s8_1^0$
17809.3	5613.5	100	2.5	$6p3_1-5d10_1^0$
17746.5	5633.4	70	1.7	$6p2_0-5d10_1^0$
17200.0	5812.4	40	1.0	$6p5_1-7s^3P_2^0$
17021.7	5873.3	100	1.7	$6p1_1-7s7_0^0$
17002.3	5880.0	200	1.8	$6p1_1-7s8_1^0$
16383.0	6102.2	70	1.2	$6p5_1-7s^1P_1^0$
15795.5	6329.2	30	−0.2	$6p1_1-5d9_2^0$
15751.5	6346.9	70		
15637.0	6393.3	100		
15586.0	6414.2	50		
15466.0	6464.0	300	1.2	$6p4_2-5d11_3^0$
15369.0	6504.9	100		
15057.0	6639.7	100	2.3	$6p1_1-5d10_1^0$
15020.0	6656.0	130		
14799.0	6755.4	60		
14670.0	6814.8	100		
14484.0	6902.3	100		
13610.0	7345.5	*1440*	0.9	$6s^1P_1^0-6p5_1$
13462.0	7426.3	*3780*	0.2	$6s^3P_1^0-6p1_1$
13351.0	7488.0	30	0.0	$5d1_2^0-7p4_2$
13322.7	7504.0	70	0.5	$5d10_1^0-4f5_2$
13083.3	7641.2	*675*	1.8	$6p3_1-6d1_2^0$
13020.3	7678.3	*1870*	0.0	$5d4_3^0-4f2_4$
13022.0*				
13002.1	7689.0	200	0.5	$5d4_3^0-4f4_2$
12983.5	7700.0	*1870*	0.0	$6s^3P_0^0-6p1_1$
12982.9*				
12936.0	7728.2	30		
12890.3	7755.7	*890*	0.8	$5d3_1^0-4f4_2$
12847.0	7781.3	*160*		
12790.0	7816.4	*370*	1.1	$5d9_2^0-4f5_2$
12535.3	7975.2	*845*	−0.6 2.9	$6s^3P_2^0-6p5_1$ and $6s^1P_1^0-6p7_2$
12336.0	8104.1	*330*	−0.6	$5d2_2^0-4f1_3$
12316.6	8117.0	*1110*	4.0	$5d2_2^0-4f4_2$
12056.3	8292.2	30		
12010.1	8324.0	*480*	1.2	$6p4_2-6d4_3^0$
11935.4	8376.2	*2540*	0.0	$6s^3P_2^0-6p6_3$
11935.3*				
11854.4	8433.4	*1060*	0.0	$6s^3P_1^0-6p2_0$
11853.3*				
11827.5	8452.6	*960*	−0.1	$6s^3P_1^0-6p3_1$
11827.2*				
11742.1	8515.3	*2580*	0.0	$6s^3P_1^0-6p4_2$
11741.9*				
11693.8	8549.2	*250*	−0.5	$6s^1P_1^0-6p8_2$ also Potassium

TABLE I (*Continued*)

Wave-lengths (I. A.)	Wave-numbers (vacuum)	Int.	$\nu_{calc}-\nu_{obs}$	Assignments
11671.6 11672.6*	8565.2	*760*	−0.2	$5d1_2^0-4f1_3$
11652.0	8579.8	125	2.7	$5d1_2^0-4f4_2$
11617.7 11618.0*	8605.0	*2000*	1.4	$6s^3P_2^0-6p7_2$
11533.3	8668.1	30	0.9	$6p1_1-6d1_2^0$
11457.5 11457.3*	8725.7	*2000*	0.3	$6s^3P_0^0-6p3_1$
11340.0 11339.4*	8816.3	*170*		
11279.5 11279.2*	8863.2	*560*	0.0	$6s^1P_1^0-6p9_0$
11216.8	8912.8	80		
11194.1 11194.0*	8931.0	*700*	0.0	$6s^1P_1^0-6p10_1$
10942.0	9136.6	30	−0.6	$6p1_1-6d3_1^0$
10895.1 10896.0*	9176.0	*540*	1.0	$6s^3P_2^0-6p8_2$
10809.5 10808.8*	9248.6	*110*		
10705.0	9338.9	30	1.6	$5d5_2^0-4f5_2$
10457.1 10458.6*	9560.4	*250*	−1.1	$6s^3P_2^0-6p10_1$
9852.1 9852.5*	10147.4	125		
9808.7*	10192.3	—	−0.3	$5d4_3^0-5f4_2$
9746.0*	10257.9	40	1.1	$5d3_1^0-5f4_2$
9414.9*	10618.6	30	4.9	$5d2_2^0-5f4_2$
9018.9**	11084.8	(1)	0.2	$5d1_2^0-5f4_2$
8552.6**	11689.1	(7)30	0.0	$6s^3P_1^0-6p5_1$
8391.3**	11913.9	(2)	−2.4	$5d4_3^0-4f5_2$
8357.03**	11962.7	(4)	−0.1	$6s^3P_0^0-6p5_1$
8345.38**	11979.4	(1)	−1.1	$5d3_1^0-4f5_2$
8114.06**	12320.9	(7)	0.0	$6s^3P_1^0-6p7_2$
8100.42**	12341.7	(2)	1.3	$5d2_2^0-4f5_2$
7808.25**	12803.4	(1)	1.1	$5d1_2^0-4f5_2$
7754.94**	12891.5	(2)	−0.1	$6s^3P_1^0-6p8_2$
7685.29**	13008.3	(1)	−0.1	$6s^1P_1^0-4f4_2$
6444.83**	15512.0	(2)	−1.3	$6s^1P_1^0-5f4_2$
6149.67**	16256.6	(6)	0.1	$6s^3P_1^0-7p4_2$
5801.79**	17231.3	(1)	−1.1	$6s^1P_1^0-4f5_2$
5761.77**	17351.0	(2)	0.0	$6s^3P_1^0-4f4_2$
2148.71	46524.8	(3)	−0.8	$5p^{2\,3}P_1-7s7_0^0$

* Previous measurements of Randall[7]
** Measurements of Walters[9]

level $5p6p6_3$ was expected to combine strongly with $5p6s\,^3P_2{}^0$. Also $5p6p9_0$ was expected to combine with $5p6s\,^1P_1{}^0$ but with less intensity. However there remained still to be classified, including the above two lines, six fairly strong infrared lines as well as several others of somewhat smaller intensity.

In order to account for the rest of these strong lines the levels of the configuration $5p(^2P_{1/2})4f$ were then sought. There were to be expected four of these levels with $J=2$, 3, 3, 4 which should combine with the $5p(^2P_{1/2})5d$ set to give eleven lines. Also transitions from the $5p4f$ set to the $5p6s$ set are possible by two-electron jumps. These four $4f$ levels were expected to lie fairly close together.

A level was found having the relative term value 52265.5 cm^{-1} and $J=2$ which combines with all four of the $5p(^2P_{1/2})5d$ levels to give infrared lines. It also combines with $5p6s\,^3P_1{}^0$ and $5p6s\,^1P_1{}^0$ giving photographically measured lines. Another level having $J=2$ and relative term value 54768.0 cm^{-1} was found which also combines with the four $5p(^2P_{1/2})5d$ levels and with $5p6s\,^1P_1{}^0$. These levels were assumed to be the $5p(^2P_{1/2})4f4_2$ and $5p(^2P_{1/2})5f\,4_2$ respectively. Fitting these two levels to a Rydberg series assigns to them the absolute term values 6926.5 cm^{-1} and 4424.0 cm^{-1}. As is to be expected these term values are quite hydrogenic being equal to $R/(3.980)^2$ and $R/(4.980)^2$ respectively. The absolute term value of the lowest level of SnI thus becomes 59192.0 cm^{-1}, a value 498 cm^{-1} smaller than that given by Green and Loring.

The calculated frequencies of the combinations of the $5p4f\,4_2$ level with $5p6s\,^3P_1{}^0$, $5p6s\,^1P_1{}^0$, and $5p5d\,3_1{}^0$ are in good agreement with the observed frequencies. In the case however of the combinations of $5p4f\,4_2$ with $5p5d\,1_2{}^0$ and $5p5d\,2_2{}^0$ the calculated frequencies are a few units higher than the observed values. This points definitely to the fact that the $5p4f\,3_3$ level must lie several units below $5p4f\,4_2$ so that combinations of both these levels with a single $5p5d$ level give lines so close as to be unresolved with the apparatus used. The $5p4f\,1_3$ level was found by means of its combinations with $5p5d\,1_2{}^0$ and $5p5d\,2_2{}^0$. Its combination with $5p5d\,4_3{}^0$ gives a calculated frequency so close to the strong line ν7678 cm^{-1} that it is undoubtedly obscured by it. The $5p4f\,2_4$ level was expected to lie close to the other $4f$ levels and to combine with $5p5d\,4_3{}^0$ to give a quite strong line. The only unclassified line which fulfills these conditions is ν7678 cm^{-1} and so it may safely be assigned this origin. This fixes the term value of $5p4f\,2_4$ at 6937.7 cm^{-1}.

There now remained two unclassified strong lines, ν8376 cm^{-1} of strength 2540 and ν8863 of strength 560. As there apparently remained but the two possible origins, viz, the previously mentioned $5p6s\,^3P_2{}^0-5p6p\,6_3$ and $5p6s\,^1P_1{}^0-5p6p\,9_0$, the lines were given these respective classifications thus fixing the values of the $5p6p\,6_3$ and $5p6p\,9_0$ levels.

Another high level was found (term value 2704.5 cm^{-1}, designation $5p(^2P_{1\frac{1}{2}})4f\,5_2$ which combines with the four $5p(^2P_{1/2})5d$ levels and with $5p6s\,^1P_1{}^0$. Obviously this is one of the $5p(^2P_{1\frac{1}{2}}4f$ levels since its separation from the mean of the $5p(^2P_{1/2})4f$ levels is very close to the $5s^25p\,^2P_{\frac{1}{2},1\frac{1}{2}}$ separation of SnII, and since it also combines with several of the $5p(^2P_{1\frac{1}{2}})5$ levels to give observed infrared lines.

TABLE II. *Term Values of Sn I.*

Normal $5s^25p^2$	$^3P_0$ 59192.0	$^3P_1$ 57500.0	$^3P_2$ 55764.0	$^1D_2$ 50578.5	$^1S_0$ 42029.0			
$5s^25p(^2P_{\frac{1}{2}})6s$	$^3P_0{}^0$ 24551.0	$^3P_1{}^0$ 24277.5	$5s^25p(^2P_{1\frac{1}{2}})6s$ $7s$	$^3P_2{}^0$ 20563.0 6775.	$^1P_1{}^0$ 19934.7 6485.			
$5s^25p(^2P_{\frac{1}{2}})6p$ $7p$	1_1 16851.0* 8436.0	2_0 15844.1* 8347.6	3_1 15825.0 8078.5	4_2 15762.2* 8021.0*				
$5s^25p(^2P_{\frac{1}{2}})5d$ $6d$	$^3D_2{}^0$ $1_2{}^0$ 15509.0 8182.	$^3F_2{}^0$ $2_2{}^0$ 15047.5 8029.	$^3D_1{}^0$ $3_1{}^0$ 14683.0 7715.	$^3F_3{}^0$ $4_3{}^0$ 14616.0 7437.	†			
$5s^25p(^2P_{1\frac{1}{2}})6p$	5_1 12588.4*	6_3 12187.2*	7_2 11956.6*	8_2 11386.0*	9_0 11071.5*	10_1 11003.7*		
$5s^25p(^2P_{1\frac{1}{2}})5d$ and $5s^25p(^2P_{\frac{1}{2}})7s$	$^1D_2{}^0$ $5_2{}^0$ 12045.	$^3D_3{}^0$ $6_3{}^0$ 11704.	$7_0{}^0$ 10976.*	$^3P_1{}^0$ $8_1{}^0$ 10969.2	$^3P_2{}^0$ $9_2{}^0$ 10522.	$^3P_1{}^0$ $10_1{}^0$ 10209.	$^1F_3{}^0$ $11_3{}^0$ 9297.	$^1P_1{}^0$ † $12_1{}^0$ 9065.
$5s^25p(^2P_{\frac{1}{2}})4f$ $5f$	1_3 6944.*	2_4 6937.7*	3_3 —	4_2 6926.5* 4424.0*				
$5s^25p(^2P_{1\frac{1}{2}})4f$	5_2 2704.5*							

† Old Notation * New Levels

The levels designated in this work as $[5p(^2P_{1/2})7s$ and $5p(^2P_{1\frac{1}{2}})5d]8_1{}^0$ and $10_1{}^0$ were given the designations $5p(^2P_{1/2})7s\,^3P_1{}^0$ and $5p(^2P_{1\frac{1}{2}})5d\,^3P_1{}^0$ respectively by Green and Loring while Back classified them in the reverse order. In cases such as this when the levels of two odd or two even configurations intermingle there is no real significance in assigning a level either to one or to the other of the configurations since in a manner of speaking it belongs to both. Even the *g*-sum rule no longer holds in such cases, and no considerations of positions of levels or of intensities of lines can be made criterions for the assignment of the level to a particular one of the configurations.

The only new level of odd configuration found in this work is that designated $[5p(^2P_{1/2})7s$ and $5p(^2P_{1\frac{1}{2}})5d]7_0{}^0$, which lies quite close to the $8_1{}^0$ level of this set.