THE SECOND SPARK SPECTRUM OF ANTIMONY AND A NOTE ON THE FIRST SPARK SPECTRUM OF TIN

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Abstract

Some sixty lines of the vacuum spark spectrum of antimony have been classified as transitions between the following terms of Sb III: $(s^25p)^2P$, $(s^26p)^2P$, $(s^26s)^2S$, $(s^27s)^2S$, $(s^28s)^2S$, $(s^25d)^2D$, $(s^26d)^2D$, $(s^24f)^2F$, $(s^25f)^2F$, $(s^25g)^2G$, $(s^26g)^2G$, $(s5p^2)^4P$, ^2D, ^2S, ^2P and $(5p^3)^4S$. Corresponding to the deepest term value an ionization potential of approximately 24.7 volts is calculated. A note on SN II gives the terms ^4P and ^2S from the $(s5p^2)$ configuration and new value for the terms: $(s^27s)^2S$, $(s^28s)^2S$, $(s^27d)^2D$ and $(s^26f)^2F$.

THE vacuum spark spectrum of antimony has been measured over the range 6600 to 600A and also the Paschen hollow-cathode spectrum from 5200 to 1950A. By means of these two measurements it has been possible to separate the first and second spark spectra rather definitely from one another and thus to arrive at a classification for the latter. Work on the first spark spectrum is now in progress and will be reported on later. The measurements of the vacuum spark spectrum below 2500A were made on a two-meter grating mounted in a vacuum spectrograph giving a dispersion of 4.5A per mm. Above 2000A several instruments were used. The vacuum spark and hollow cathode spectra were measured in Edmonton on a two-meter Rowland grating kindly loaned to the author by Professor Smith. The vacuum spark spectrum was also measured in Michigan by the author using a Hilger E_2 quartz spectrograph made available through the courtesy of the Department of Physics. The author is also indebted to Professor R. A. Sawyer of Michigan for a plate of the vacuum spark in the region from 5300 to 6600A made on a large Hilger glass spectrograph. A few wave-lengths are taken also from Schippers measures given by Kayser.

In a previous report[1] the author gave three multiplets for Sb III all of which turn out to be real but the first one given was improperly classified as $(s^26s)^2S—(s^26p)^2P$. It should have been $(s5p^2)^2S-(s^26p)^2P$. It thus corresponds very satisfactorily to the doublet in As III at 4200A. A paper on As III and Sb III appeared later in the Indian Journal of Physics.[2]

Some important electron configurations and resultant terms expected in the spectrum of Sb III are as follows:

[1] Lang, Phys. Rev. **32**, 737 (1928).
[2] Pattabhiramiah and Rao, Indian Journ. Phys. **3**, 437, 1929

Configuration	Terms	Configuration	Terms
$(s^2 5p)$	^2P	$(s5p^2)$	^4P, ^2PDS
$(s^2 6s)$	^2S	$(s5p5d)$	^4PDF, ^2PDF
$(s^2 5d)$	^2D	$(s5p6s)$	$^4P ^2P$
$(s^2 4f)$	^2F	$(5p^3)$	^4S, ^2PD
$(s^2 5g)$	^2G	$(s5p6p)$	^4PSD, ^2SPD

TABLE I. *Empirical term values in Sb III.*

Odd Terms			Even Terms		
$(s^2 5p)^2P_{\frac{1}{2}}$	200272	6576	$(s5p^2)^2D_{1\frac{1}{2}}$	123744	1270
$(s^2 5p)^2P_{1\frac{1}{2}}$	193696		$(s5p^2)^2D_{2\frac{1}{2}}$	122474	
$(s^2 4f)^2F_{2\frac{1}{2}}$	118940	373	$(s^2 6s)^2S_{\frac{1}{2}}$	107321	
$(s^2 4f)^2F_{3\frac{1}{2}}$	118567		$(s5p^2)^2S_{\frac{1}{2}}$	106852	
$(s^2 6p)^2P_{\frac{1}{2}}$	85550	1668	$(s5p^2)^2P_{\frac{1}{2}}$	105624	5392
$(s^2 6p)^2P_{1\frac{1}{2}}$	83882		$(s5p^2)^2P_{1\frac{1}{2}}$	100232	
$(s^2 5f)^2F_{3\frac{1}{2}}$	64055	−55	$(s^2 5d)^2D_{1\frac{1}{2}}$	101450	1567
$(s^2 5f)^2F_{2\frac{1}{2}}$	64000		$(s^2 5d)^2D_{2\frac{1}{2}}$	99883	
$(5p^3)^4S_{1\frac{1}{2}}$	51259		$(s^2 7s)^2S_{\frac{1}{2}}$	57143	
			$(s^2 6d)^2D_{1\frac{1}{2}}$	55589	237
Even Terms			$(s^2 6d)^2D_{2\frac{1}{2}}$	55352	
$(s5p^2)^4P_{\frac{1}{2}}$	145906	3596	$(s^2 8s)^2S_{\frac{1}{2}}$	36882	
$(s5p^2)^4P_{1\frac{1}{2}}$	142310	5358	$(s^2 5g)^2G$	35966	
$(s5p^2)^4P_{2\frac{1}{2}}$	136952		$(s^2 6g)^2G$	25812	

TABLE II. *Comparison of term values.*

Term	Element	4	5	6	7	8
^2S	In I			22295	10366	6031
	Sn II			15205	7841	5194
	Sb III			11924	6349	4098
$^2P_{\frac{1}{2}}$	In I		46668	14811	7808	
	Sn II		29426	11553		
	Sb III		22252	9506		
$^2D_{1\frac{1}{2}}$	In I		13775	7620	4832	
	Sn II		11575	6867	4342	
	Sb III		11272	6176		
$^2F_{2\frac{1}{2}}$	In I		6960			
	Sn II		7104	4511		
	Sb III	13215	7111			
^2G	In I					
	Sn II					
	Sb III		3996	2868		

TABLE III. *Combinations, intensities and discrepancies in the spectrum of Sb III.*

Even Terms \ Odd Terms	$(s^25p)^2P_{\frac{1}{2}}$ 200272	$(s^25p)^2P_{1\frac{1}{2}}$ 193696	$(s^24f)^2F_{2\frac{1}{2}}$ 118940	$(s^24f)^2F_{3\frac{1}{2}}$ 118567	$(s^26p)^2P_{\frac{1}{2}}$ 85550	$(s^26p)^2P_{1\frac{1}{2}}$ 83882	$(s^25f)^2F_{3\frac{1}{2}}$ 64055	$(s^25f)^2F_{2\frac{1}{2}}$ 64000	$(5p^3)^4S_{1\frac{1}{2}}$ 51259
$(s5p^2)^4P_{\frac{1}{2}}$ 145906	12 2	2 1							10 −2
$(s5p^2)^4P_{1\frac{1}{2}}$ 142310	15 −2	10 −2							10 −4
$(s5p^2)^4P_{2\frac{1}{2}}$ 136952		12 0							12 0
$(s5p^2)^2D_{1\frac{1}{2}}$ 123744	20 1	10 −1			12 5	5 3		15 −3	8 1
$(s5p^2)^2D_{2\frac{1}{2}}$ 122474		20* −6				15 5	15 −2	3 −3	20* 1
$(s^26s)^2S_{\frac{1}{2}}$ 107321	30 1	40 0			30 0	40 0			
$(s5p^2)^2S_{\frac{1}{2}}$ 106852	20 0	30 0			30 0	50 0			
$(s5p^2)^2P_{\frac{1}{2}}$ 105624	10 −3	10 0							
$(s^25d)^2D_{1\frac{1}{2}}$ 101450	40 −2	20 0	1 −4	3 −15?	3 0	1 −1		20 0	
$(s5p^2)^2P_{1\frac{1}{2}}$ 100232	15 −2	20 0							
$(s^25d)^2D_{2\frac{1}{2}}$ 99883		40 4	1 −6			5 3	20 0	5 1	
$(s^27s)^2S_{\frac{1}{2}}$ 57143	10 −3	15 −3			15 1	30 −1			
$(s^26d)^2D_{1\frac{1}{2}}$ 55589	10 −3	8 −2			20 1	15 0			
$(s^26d)^2D_{2\frac{1}{2}}$ 55352		15 −4				50 0			
$(s^28s)^2S_{\frac{1}{2}}$ 36882					3 0	5 0			
$(s^25g)^2G$ 35966			50 0	50 0			40 −1	40 −1	
$(s^26g)^2G$ 25812			5 3	5 0			1 −2	1 3	

* Classified twice.

TABLE IV. *Classified lines of Sb III.*

Classification	λ(I.A.)	I	ν
$(s^25p)^2P_{\frac{1}{2}}-(s^26d)^2D_{1\frac{1}{2}}$	691.18	10	144680
$^2P_{1\frac{1}{2}}-\ {}^2D_{2\frac{1}{2}}$	722.86	15	138340
$^2P_{1\frac{1}{2}}-\ {}^2D_{1\frac{1}{2}}$	724.81	8	138105
$(s^25p)^2P_{\frac{1}{2}}-(s^27s)^2S_{\frac{1}{2}}$	698.69	10	143126
$^2P_{1\frac{1}{2}}-\ {}^2S_{\frac{1}{2}}$	732.33	15	136550
$(s^25p)^2P_{\frac{1}{2}}-(s5p^2)^2P_{1\frac{1}{2}}$	999.62	15	100038
$^2P_{\frac{1}{2}}-\ {}^2P_{\frac{1}{2}}$	1056.58	10	94645
$^2P_{1\frac{1}{2}}-\ {}^2P_{1\frac{1}{2}}$	1069.93	20	93464
$^2P_{1\frac{1}{2}}-\ {}^2P_{\frac{1}{2}}$	1135.43	10	88072
$(s^25p)^2P_{\frac{1}{2}}-(s^25d)^2D_{1\frac{1}{2}}$	1011.94	40	98820
$^2P_{1\frac{1}{2}}-\ {}^2D_{2\frac{1}{2}}$	1065.90	40	93817
$^2P_{1\frac{1}{2}}-\ {}^2D_{1\frac{1}{2}}$	1084.06	20	92246
$(s^25p)^2P_{\frac{1}{2}}-(s5p^2)^2S_{\frac{1}{2}}$	1070.43	20	93420
$^2P_{1\frac{1}{2}}-\ {}^2S_{\frac{1}{2}}$	1151.49	30	86844
$(s5p^2)^4P_{2\frac{1}{2}}-(5p^3)^4S_{1\frac{1}{2}}$	1056.58	10	94645
$^4P_{1\frac{1}{2}}-\ {}^4S_{1\frac{1}{2}}$	1098.34	10	91047
$^4P_{\frac{1}{2}}-\ {}^4S_{1\frac{1}{2}}$	1166.96	12	85693
$(s^24f)^2F_{2\frac{1}{2}}-(s^26g)^2G$	1073.76	5	93131
$^2F_{3\frac{1}{2}}-\ {}^2G$	1078.10	5	92755
$(s^25p)^2P_{\frac{1}{2}}-(s^26s)^2S_{\frac{1}{2}}$	1075.82	30	92952
$^2P_{1\frac{1}{2}}-\ {}^2S_{\frac{1}{2}}$	1157.74	40	86375
$(s^24f)^2F_{2\frac{1}{2}}-(s^25g)^2G$	1205.20	50	82974
$^2F_{3\frac{1}{2}}-\ {}^2G$	1210.64	50	82601
$(s^25p)^2P_{\frac{1}{2}}-(s5p^2)^2D_{1\frac{1}{2}}$	1306.69	20	76529
$^2P_{1\frac{1}{2}}-\ {}^2D_{2\frac{1}{2}}$	1404.18	20	71216
$^2P_{1\frac{1}{2}}-\ {}^2D_{1\frac{1}{2}}$	1429.57	10	69951
$(s5p^2)^2D_{1\frac{1}{2}}-(5p^3)^4S_{1\frac{1}{2}}$	1379.58	8	72486
$^2D_{2\frac{1}{2}}-\ {}^4S_{1\frac{1}{2}}$	1404.18	20	71216
$(s5p^2)^2D_{1\frac{1}{2}}-(s^25f)^2F_{2\frac{1}{2}}$	1673.89	15	59741
$^2D_{2\frac{1}{2}}-\ {}^2F_{2\frac{1}{2}}$	1710.23	3	58472
$^2D_{2\frac{1}{2}}-\ {}^2F_{3\frac{1}{2}}$	1711.84	15	58417
$(s^25p)^2P_{\frac{1}{2}}-(s5p^2)^4P_{1\frac{1}{2}}$	1725.33	15	57960
$^2P_{1\frac{1}{2}}-\ {}^4P_{2\frac{1}{2}}$	1762.30	12	56744
$^2P_{\frac{1}{2}}-\ {}^4P_{\frac{1}{2}}$	1839.32	12	54368
$^2P_{1\frac{1}{2}}-\ {}^4P_{1\frac{1}{2}}$	1946.13	10	51384
$^2P_{1\frac{1}{2}}-\ {}^4P_{\frac{1}{2}}$	2091.85	2	47791
$(s^26p)^2P_{\frac{1}{2}}-(s^28s)^2S_{\frac{1}{2}}$	2054.10	3	48668
$^2P_{1\frac{1}{2}}-\ {}^2S_{\frac{1}{2}}$	2127.00	5	47000
$(s5p^2)^2D_{1\frac{1}{2}}-(s^26p)^2P_{1\frac{1}{2}}$	2507.71	5	39865
$^2D_{2\frac{1}{2}}-\ {}^2P_{1\frac{1}{2}}$	2590.13	15	38597
$^2D_{1\frac{1}{2}}-\ {}^2P_{\frac{1}{2}}$	2617.17	12	38199
$(s^25f)^2F_{3\frac{1}{2}}-(s^26g)^2G$	2614.20	1	38241
$^2F_{2\frac{1}{2}}-\ {}^2G$	2617.63	1	38191
$(s^25d)^2D_{1\frac{1}{2}}-(s^25f)^2F_{2\frac{1}{2}}$	2669.39	20	37450
$^2D_{2\frac{1}{2}}-\ {}^2F_{2\frac{1}{2}}$	2785.87	5	35884
$^2D_{2\frac{1}{2}}-\ {}^2F_{3\frac{1}{2}}$	2790.27	20	35828

TABLE IV (*Continued*)

Classification	λ(I.A.)	I	ν
$(s^26p)^2P_{\frac{1}{2}}-(s^26d)^2D_{1\frac{1}{2}}$	3336.61	20	29962
$^2P_{1\frac{1}{2}}-\quad ^2D_{2\frac{1}{2}}$	3504.07	50	28530
$^2P_{1\frac{1}{2}}-\quad ^2D_{1\frac{1}{2}}$	3533.45	15	28293
$(s^26p)^2P_{\frac{1}{2}}-(s^27s)^2S_{\frac{1}{2}}$	3519.06	15	28408
$^2P_{1\frac{1}{2}}-\quad ^2S_{\frac{1}{2}}$	3738.90	30	26738
$(s^25f)^2F_{3\frac{1}{2}}-(s^25g)^2G$	3559.18	40	28088
$^2F_{2\frac{1}{2}}-\quad ^2G$	3566.25	40	28033
$(s^26s)^2S_{\frac{1}{2}}-(s^26p)^2P_{1\frac{1}{2}}$	4265.09	40	23439
$^2S_{\frac{1}{2}}-\quad ^2P_{\frac{1}{2}}$	4591.89	30	21771
$(s5p^2)^2S_{\frac{1}{2}}-(s^26p)^2P_{1\frac{1}{2}}$	4352.16	50	22970
$^2S_{\frac{1}{2}}-\quad ^2P_{\frac{1}{2}}$	4692.91	30	21302
$(s^24f)^2F_{2\frac{1}{2}}-(s^25d)^2D_{2\frac{1}{2}}$	5247.71	1	19051
$^2F_{2\frac{1}{2}}-\quad ^2D_{1\frac{1}{2}}$	5717.3	1	17486
$^2F_{3\frac{1}{2}}-\quad ^2D_{1\frac{1}{2}}$	5845.5	3	17102
$(s^25d)^2D_{1\frac{1}{2}}-(s^26p)^2P_{1\frac{1}{2}}$	5690.8	1	17567
$^2D_{2\frac{1}{2}}-\quad ^2P_{1\frac{1}{2}}$	6246.7	5	16004
$^2D_{1\frac{1}{2}}-\quad ^2P_{\frac{1}{2}}$	6287.6	3	15900

In Table I the terms which have been located together with the empirical term values and separations are given. All of the term values rest upon an arbitrary choice of 64000 cm^{-1} for the value of $(s^25f)^2F_{2\frac{1}{2}}$. Experience has shown that one can probably arrive at as good or even better values for the terms by a comparison such as is given in Table II than by the use of a Rydberg formula applied to two P or two S terms such as are available in this instance. The deepest F terms are not absolutely certain since the combination with the deepest normal D terms is not very satisfactory. The same may also be true of the second G terms and the third S terms, the last depending upon one combination only since no others fall within the range of measurements. Hence until some of these terms can be established more certainly it seemed as well to estimate the value of the basic term.

In Table III the intensities of observed combinations are shown and under each intensity the discrepancy between the observed wave-number and the wave-number calculated from the values assigned to the energy levels is given. In Table IV a list of all the lines which have been classified in the spectrum of Sb III is given. Throughout this report all wave-lengths above 2000A are given in I.A. (air) below this value in I.A. (vacuum) while all wave-numbers are reduced to vacuum values. Corresponding to the deepest term of this spectrum an ionization potential of 24.7 volts is found.

A NOTE ON SN II

The hollow cathode spectrum of tin was also photographed between 6000A and 2000A in an endeavor to find more terms from the $(s5p^2)$ configuration. Out of the total of nine terms (^4P, ^2D, ^2S, ^2P) arising from this configuration none but ^2D had been located.[3]

The $(s^25p)^2P-(s5p^2)^4P$ multiplet in In I had already been found[4] and those for Sn II and Sb III were located by the use of the doublet laws. The multiplet in Sn II is taken from the spectrum of the hollow cathode. It occurs but very weakly in the vacuum spark spectrum. That for Sb III is taken from the vacuum spark spectrum and the only abnormality is the weak intensity of one of the lines in this multiplet.

TABLE V. *Multiplets and terms in the spectrum of Sn II.*

Configuration	λ(I.A.)	I	ν	Δν	Term values	
$(s^25p)^2P_{\frac{1}{2}}-(s^27s)^2S_{\frac{1}{2}}$	1158.21	2	86340		$(s^25p)^2P_{\frac{1}{2}}$	117704
$^2P_{1\frac{1}{2}}-\ ^2S_{\frac{1}{2}}$	1218.19	4	82089	4251	$^2P_{1\frac{1}{2}}$	113451*
$(s^26p)^2P_{\frac{1}{2}}-(s^28s)^2S_{\frac{1}{2}}$	3930.37	2	25435		$(s^27s)^2S_{\frac{1}{2}}$	31363
$^2P_{1\frac{1}{2}}-\ ^2S_{\frac{1}{2}}$	4071.79	2	24552	883		
$(s^25d)^2D_{1\frac{1}{2}}-(s^26f)^2F$	3537.56	1	28260			
$^2D_{2\frac{1}{2}}-\ ^2F$	3620.54	1	27613	647	$(s^28s)^2S_{\frac{1}{2}}$	20778
$(s^25p)^2P_{1\frac{1}{2}}-(s5p^2)^2D_{1\frac{1}{2}}$	1699.50	12	58841	4252	$(s^27d)^2D_{1\frac{1}{2}}$	17367
$^2P_{1\frac{1}{2}}-\ ^2D_{2\frac{1}{2}}$	1811.23	15	55211	622*	$^2D_{2\frac{1}{2}}$	17327
$^2P_{\frac{1}{2}}-\ ^2D_{1\frac{1}{2}}$	1831.85	12	54589			
$(s5p^2)^2D_{1\frac{1}{2}}-(s^26f)^2F$	2448.93	1	40821		$(s^26f)^2F$	18043
$^2D_{2\frac{1}{2}}-\ ^2F$	2486.95	2	40197	624		
					$(s5p^2)^4P_{\frac{1}{2}}$	73196
$(s^25p)^2P_{\frac{1}{2}}-(s5p^2)^4P_{1\frac{1}{2}}$	2151.57	12	46462		$^4P_{1\frac{1}{2}}$	71242
$^2P_{1\frac{1}{2}}-\ ^4P_{2\frac{1}{2}}$	2209.70	10	45241	1954	$^4P_{2\frac{1}{2}}$	68210
$^2P_{\frac{1}{2}}-\ ^4P_{\frac{1}{2}}$	2246.11	10	44508			
$^2P_{1\frac{1}{2}}-\ ^4P_{1\frac{1}{2}}$	2368.26	15	42211	1957	$(s5p^2)^2D_{1\frac{1}{2}}$	58863
$^2P_{1\frac{1}{2}}-\ ^4P_{\frac{1}{2}}$	2483.48	12	40254		$^2D_{2\frac{1}{2}}$	58240*
$(s^25p)^2P_{\frac{1}{2}}-(s5p^2)^2S_{\frac{1}{2}}$	1223.73	10	81717			
$^2P_{1\frac{1}{2}}-\ ^2S_{\frac{1}{2}}$	1290.89	20	77465	4252	$(s5p^2)^2S_{\frac{1}{2}}$	35986
$(s^26p)^2P_{\frac{1}{2}}-(s^27d)^2D_{1\frac{1}{2}}$	3465.73	3	28846	884		
$^2P_{1\frac{1}{2}}-\ ^2D_{2\frac{1}{2}}$	3570.09	8	28002			
$^2P_{1\frac{1}{2}}-\ ^2D_{1\frac{1}{2}}$	3575.31	4	27962	40		

* Green and Loring.

The $(s^25p)^2P-(s5p^2)^2D$ multiplet seems well established in Sn II and Sb III. One peculiarity worth mentioning is that the position of this multiplet in the spectrum of Sn II is almost exactly the same as in Si II[5]. However, there seems little doubt that in Sn II this group has been correctly classified[3] for when a tin spark in nitrogen, excited by a 2200 volt transformer joined to the 110 volt A.C. mains, was photographed between 2000A and 1250A but nine tin lines were found including the three lines of this multiplet, and every one of these lines except one (1290.90A) had been classified as arising from transitions involving the deepest ^2P levels of the atom of Sn II.

[3] Green and Loring, Phys. Rev. **30,** 574 (1927).

[4] Lansing, Phys. Rev. **34,** 597 (1929); Sawyer and Lang, Phys. Rev. **34,** 712 (1929).

[5] Fowler, Trans. Roy. Soc. **A225,** 26 (1925).

In regard to the $(s^2 5p)^2P-(s5p^2)^2S$ doublet it may be stated that the line (1290.90A) together with another line at 1223.79A which occurs in the vacuum spark, but unable here to pass the fluorite window, have the separation of the deepest ^2P terms. There seems little doubt that these two lines represent this doublet as has been suggested.[3]

The remaining $(s^2 5p)^2P-(s5p^2)^2P$ multiplet in Sn II has not been located with any certainty. There is one possibility worth mentioning, however. The $(s^2 5p)^2P-(s^2 7s)^2S$ doublet[3] occurs with too great intensity in the vacuum spark and the ^2S term is greater than one would expect. Another pair of weaker lines, one of which had not been resolved from a stronger tin line, probably represent this doublet and the stronger pair represents one-half of the missing multiplet. However, it must be said that there is not complete agreement yet between Sn II and Sb III in regard to these terms of the $(s5p^2)$ configuration and it does not seem possible to obtain this at the present time. When the arc spectrum of indium has been studied below 2000A it should be possible to obtain this agreement. An attempt to do this is now in progress. One or two other minor alterations have been made in the spectrum of Sn II all of which are shown in Table V.

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