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THE SPECTRUM OF DOUBLY-IONISED ANTIMONY.

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Plate VII.

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ABSTRACT.—While investigating the structure of the spectra of Te III and I IV, a comparison of these spectra with those due to Sn I and Sb II was made by the author, as these form an iso-electronic sequence. This comparison led to a modification and extension of the analysis of Sb II due to Lang and Vestine. A large number of the levels were assigned to the proper configurations and a few new terms discovered.

§ 1. INTRODUCTION.

While working on the spectra of doubly-ionised tellurium [1] and trebly-ionised iodine,[2] the author found it necessary to make a close comparative study of the row of iso-electronic spectra, Sn I, Sb II, Te III, and I IV. Such a study revealed the necessity of certain modifications in the analysis of Sb II reported by Lang and Vestine,[3] and it is the purpose of the present paper to record those changes with special reference to the $6p$ terms, the previous assignments of some of which appear improbable.

This improbability was first suggested by the abnormality in the intervals of the $6p^3D$ term identified by Lang. An examination of table I shows that these intervals are very regular in all the spectra homologous with Sb II.

Table I.

mp^3D Intervals in similar Spectra.

Spectrum.	Ge I.	As II.	Se III.	Sn I.	Sb II.	Te III.	I IV.
$6p^3D_1-{}^3D_2$	—	200·4	309·5	63	1071 + (86)	212	931
${}^3D_2-{}^3D_3$	—	2083·5	3172·0	3565	−135 + (5400)	7620	10271

+ Values due to Lang and Vestine. Those due to the present work of the author are given in parenthesis.

Further, the intensities of the lines in the $6s\,^3P-6p\,^3D$ multiplet of Sb II, as identified by the above authors also seem to be unsatisfactory. They are as shown below.

$6p$	$^3D_1$	$^3D_2$	$^3D_3$
$6s\,^3P_0$	(30)		
$^3P_1$	(12)	(12)	
$^3P_2$	(6)	(30)	(50)

The combination $6s\,^3P_1-6p\,^3D_2$ is relatively faint, and in fact fainter than $6s\,^3P_2-6p\,^3D_2$. The other important triplet term $6p\,^3P$ in Sb II was not identified by Lang. The corresponding term was, however, observed to give strong combination lines in the spectra of Te III,[4] and As II,[5] although the intervals are found to be abnormal. The latter fact probably would account for the failure to identify the term in Sb II.

The above considerations led the writer to undertake a careful reinvestigation of the spectrum of Sb II, in the light of the results he has obtained in Te III and I IV.

§ 2. EXPERIMENTAL.

The sources used in these experiments were sparks in air, and in hydrogen, between electrodes of pure antimony. The lines of Sb II are very easily excited, and appear even in the ordinary sparks in air. A large quartz Littrow spectrograph was mainly used, and the photographic plates were of the Ilford special rapid type. Lines of the iron arc served to reduce the plates and lines due to impurities were eliminated by comparison with other spectra (mainly of copper and arsenic), produced under similar conditions.

§ 3. OBSERVATIONAL

The $6p$ terms due to Lang, as well as those identified by the author in the present work, are shown in table II. If the new assignments be adopted, the intervals of the $6p\,^3D$ term are found to be in harmony with those in other spectra, as is evident from table I.

TABLE II.

Multiplets. Sb II.

Term Designation. Lang.	 Author.	Term Value	$6s\,^3P_0$ 80863·0	$^3P_1$ 80465·8	$^3P_2$ 74727·2	$^1P_1$ 74102·4
	$6p\,^3D_1$ =	63904·4 86·2	16958·6(15)	—	—	—
	$^3D_2$ =	63818·2		16647·6 (100)	—	—
$6p\,^3D_3$	$^3D_3$ =	58418·6			16308·6 (50)	
$^3D_1$	$^3P_1$ =	59354·3 1070·4	21511·8 (30)	21111·5 (12)	15372·7 (16)	14759·5 (2)
$^3D_2$	$^3P_2$ =	58283·9	22581· (2)	22181·9 (12)	16443·4 (30)	15819·0 (5)
$^3S_1$	$^3S_1$ =	57000·8		23464·6 (8)	17726·4 (30)	17102·0 (6)
Lang.	**Author**	**Term.**	$5p\,^3P_0$ 150000	$^3P_1$ 146945	$^3P_2$ 144341	$^1D_2$ 137209
(..)	$5p^3\ ^3P_1$ =	72863 −447	77136·1 (3)	74083·2 (2)		64348·9 (3)
(35)	$^3P_2$ =	73310		73635·6 (6)	71031·5 (6)	
(39)	$5d\,^1D_2$ =	71604		75335·2 (8)	72730·5 (2)	65600·4 (2)
(77)	$6d\,^3D1$ =	35950	114045·8 (4)		108389·3 (0)	
(..)	$7s\,^3P_0$ =	44775		102170 (5)		
$7s\,^3P_1$	$^3P_1$ =	44084		102857·4 (4)	100258·6 (4)	93126·3 (6)
$^3P_2$	$^3P_2$ =	38183		109300·4 (2)	106704·3 (3)	
(53)	$^1P_1$		107463 (1)	104408·1 (2)		94672·8 (8)
(37)	$5p^3\ ^3P_1$ =	72861·4 −449			15861·6 (2)	
(35)	$^3P_2$ =	73310·3	139·558 (2)			17261·2 (5)
(77)	$6d\ ^3D_1$ =	35507·2	23404·2 (10)			
(75)	$^3P_1$ =	36799·8	22557·5 (5)	21484·1 (8)	20202·5 (3)	19350 (12)
(71)	$^3P_2$ =	37597·8	21757·0 (6)	20686·1 (20)	19403·4 (5)	
(73)	$^1P_1$ =	37271·7		21012·2 (20)	19730·1 (2)	
$7s\,^3P_1$	$7s\,^3P_1$ =	44084·0	15270·3 (1)			
$^3P_2$	$^3P_1$ =	37644·8	21710·5 (15)	20059·5 (10)	19350·0 (0)	
(79)	$8s\,^3P$	21485·1		36798·2 (7)		34663·1 (3)

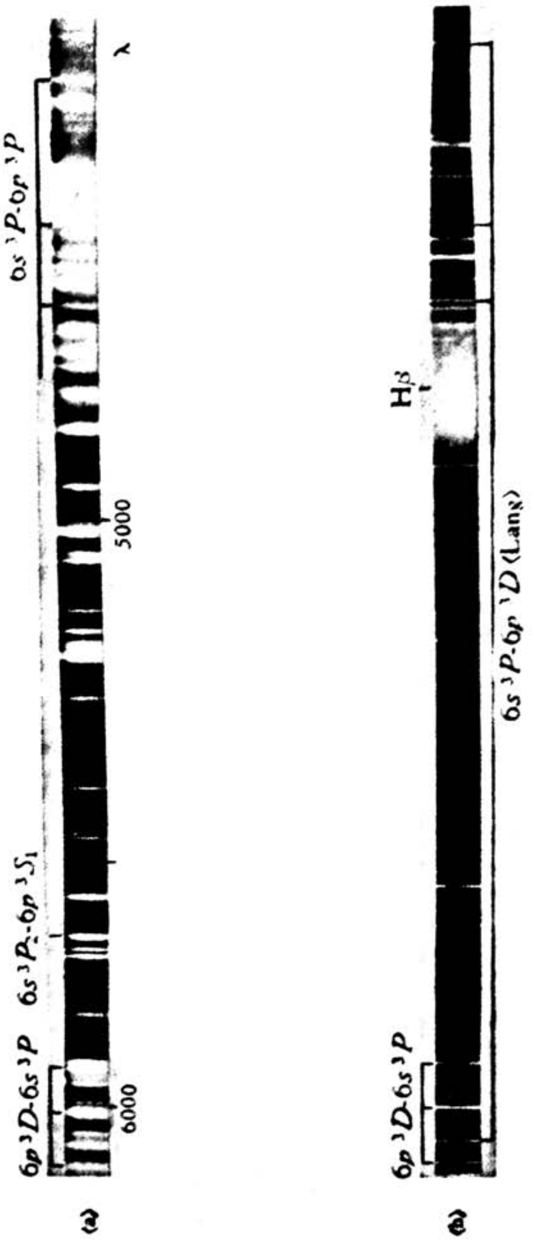
A much more striking evidence of the correctness of the above identification is seen in table III, which shows the very regular progress of the corresponding lines in Sn I-like and Ge I-like spectra so far as they are known at present.

TABLE III.

Corresponding lines in similar spectra.

Spectrum.	$6s^3P_0$-$6p^3D_1$.	$\delta\nu$	$6s^3P_1$-$6p^3D_2$.	$\delta\nu$
As II	18184	8751	17986	8754
Se III	26935		26740	
Sn I	8726	8232	8515	8133
Sb II	16958	7697	16648	7963
Te III	4655		24611	
Spectrum.	$6s^3P_1$-$6p^3P_1$.	$\delta\nu$	$6s^3P_2$-$6p^3P_1$.	$\delta\nu$
As II	20053	9526	17672	8297
Se III	29579		25969	
Sn I	11689	9423	7975	7398
Sb II	21112	12973	15373	11015
Te III	34085		26388	
Spectrum.	$6s^3P_2$-$6p^3D_3$.	$\delta\nu$	$6s^3P_0$-$6p^3P_1$.	$\delta\nu$
As II	17689	8613	19110	8892
Se II	26302		28002	
Sn I	8376	7933	11963	9549
Sb II	16309	8225	21512	12828
Te III	24534		34340	
Spectrum.	$6s^3P_1$-$6p^3P_2$.	$\delta\nu$	$6s^3P_2$-$5p^3P_2$	$\delta\nu$
As II	21131	9962	18751	8732
Se III	31093		27483	
Sn I	12321	9861	8605	7836
Se II	22182	9764	16443	7805
Te III	31956		24248	

The fine structures of some of the intense lines of the Sb II spectrum in the visible region, were recently studied by Tolansky,[6] who slightly modified the previous work of Badami.[7] The latter's work confirms the present assignment of $6p\ ^3P$ and ^3S terms. The work of Tolansky supports the assignments of $6p\ ^3D_1$ and $^3D_3$, the line ν 16958·6 yielding six fine structure components, three of which are due to one isotope (121) and the remaining, to the second isotope (123), of antimony. The interval factors of the $6p$ terms are found to be in consonance with those observed in As II, of the same chemical group.



Antimony spark spectra.

(a) Air spark.
(b) Hydrogen spark.

In addition to the $6p$ terms newly suggested by the writer, the above table of multiplets gives other terms assigned to the various electron configurations. These terms were designated by Lang and Vestine by arbitrary numbers, mentioned in the first column of the table II. As has already been pointed out, the new assignments have been suggested by a comparative study of the row of Sn-I-like spectra. The most important of these are the terms due to sp^3 inner electron configuration. It was observed previously by Rao,[8] that the values of the sp^3 terms relative to the sp^2s terms show a marked increase with increasing ionisation. The curves plotted in figures 1 to 4, illustrate this peculiar regularity. In Sn I-like spectra, the crossing over of the sp^3 and sp^2s terms occurs at the third stage of ionisation, *i.e.*, in Te III. The writer believes that this evidence afforded by these smooth curves supports strongly the assignments he has made.

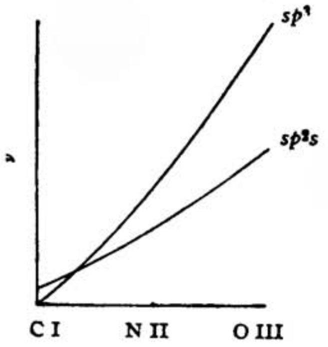


FIGURE 1.

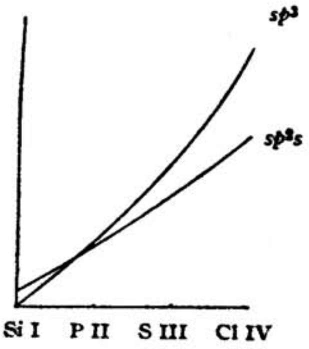


FIGURE 2.

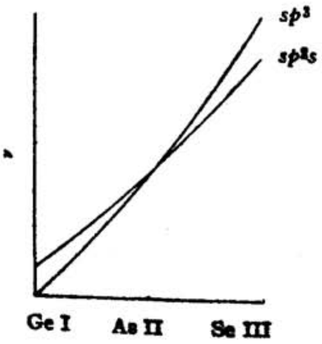


FIGURE 3.

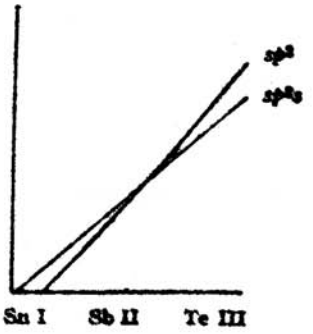


FIGURE 4.

§ 4. TERM VALUES.

The term values given in tables II and IV, are calculated from the value 150000 cm^{-1} of the deepest term $5p^3P_0$ due to Lang. The value of this term could also be calculated from the lines,

$$6s^3P_2-5p^3P_2=-69614.$$

$$^3P_2-6p^3P_2=16443.$$

It is found then equal to 151723 cms^{-1}. As no greater accuracy can be claimed for this than for the value suggested by Lang, both being obtained from the simple formula applied to two Rydberg members only, the value given by Lang and Vestine is retained in the table of terms below. The table is self-explanatory.

TABLE IV.

Terms in Sb II.

Term		Value	Term		Value
Lang	Author		Lang	Author	
$6s\,^3P_0$	Same	80863·0	(37)	$sp^3\,^3P_1$	72861·4
$^3P_1$	,,	80465·8	(35)	$^3P_2$	73310·3
$^3P_2$	,,	74727·2	(77)	$6d\,^3D_1$	35507·2
$^1P_1$	,,	74102·4	(75)	$^3P_1$	36799·8
	$6p\,^3D_1$	63904·4	(71)	$^3P_2$	37597·8
	$^3D_2$	63818·2	(73)	$^1P_1$	37271·7
$6p\,^3D_3$	Same	58418·6	$7s\,^3P_1$	Same	44084·0
$^3D_1$	$6d\,^3P_1$	59354·3	$^3P_2$	,,	37644·8
$^3D_2$	$^3P_2$	58283·9	$^1P_1$	,,	38375·4
$^3S_1$	Same	57000·8	$^3P_1$	$8s\,^3P_1$	21485·1

Finally, in table V is given a catalogue oft he lines of Sb II classified in the present work. The classifications due to Lang and Vestine are also included for comparison.

TABLE V.

Classified lines in Sb II.

λ. I. A.	ν (vac)	Classification.	
		Lang.	Author.
876·84 (4)	114045	5p $^3P_0-77$	5p $^3P_0-6d\ ^3D_1$
914·91 (2)	109300	$^3P_1-7s\ ^3P_2$	Same
922·6 (0)	108389	$^3P_2-77$	5p $^3P_2-6d\ ^3D_1$
930·55 (1)	107463	$^3P_0-53$	$^3P_0-7s\ ^1P_1$
937·17 (3)	106704	$^3P_2-7s\ ^3P_2$	Same
957·78 (2)	104408	$^3P_1-53$	5p $^3P_1-7s\ ^1P_1$
972·22 (4)	102857	$^3P_1-7s\ ^3P_1$	Same
997·47 (4)	100258	$^3P_2-\ \ ^3P_1$	Same
1056·27 (8)	94672·8	$^1D_2-53$	5p $^1D_2-7s\ ^1P_1$
1073·81 (6)	93126·3	$^1D_2-7s\ ^3P_1$	Same
1196·74 (0)	83560·3	$^1S_0-53$	5p $^1S_0-7s\ ^1P_1$
1296·41 (3)	77136·1	$^3P_0-35$	$^3P_0-sp^3\ ^3P_1$
1327·40 (8)	75335·2	$^3P_1-39$	$^3P_1-5d\ ^1D_2$
1349·8 (2)	74083·2	$^3P_1-37$	$^3P_1-sp^3\ ^3P_1$
1358·0 (6)	73635·6	$^3P_1-35$	$^3P_{.}-sp^3\ ^3P_1$
1374·9 (2)	73730·5	$^3P_2-39$	$^3P_2-5d\ ^1D_2$
1407·8 (6)	71031·5	$^3P_2-35$	$^3P_2-sp^3\ ^3P_2$
1524·4 (2)	65600·4	$^1D_2-39$	$^1D_2-5d\ ^1D_2$
1554·0 (3)	64348·9	$^1D_2-37$	$^1D_2-sp^3\ ^3P_1$
1874·5 (2)	53232·9	$^1S_0-37$	$^1S_0-sp^3\ ^3P_1$
2716·72 (7)	36798·2	6p $^3D_3-79$	6p $^3P_2-8s\ ^3P_1$
2884·07 (3)	34663·1	$48-79$	$^1D_2-$,,
3001·70 (3)	33304·8	6p $^1S_0-79$	$^1S_0-$,,
3520·47 (12)	28397·2	……	$^3D_1-6d\ ^3D_1$
3893·75 (8)	25674·9	6s $^3P_1-6p\ ^1S_0$	Same
3929·23 (4)	25443·0	$15-48$	$^3D_2-7s\ ^1P_1$
4111·2 (4)	24316·7	6s$^3P_1-6p^1D_2$	Same
4260·55 (8)	23464·6	,, $-^3S_1$	Same
4271·54 (10)	23404·2	6p $^3D_1-77$	$^3P_1-6d\ ^3D_1$
4427·25 (3)	22581·1	6s $^3P_0-6p^3D_2$ (?)	6s $^3P_0-6p\ ^3P_2$
4431·87 (5)	22557·5	6p $^3D_1-75$	6p $^3P_1-6d\ ^3P_1$
4506·92 (12)	22181·9	6s $^3P_1-6p^3D_2$	6s $^3P_1-6p\ ^3P_2$
4594·93 (6)	21757·0	6p $^3D_1-71$	6p $^3P_1-6d\ ^3P_2$
4604·77 (15)	21710·5	,, $-7s\ ^3P_2$	,, $-7s\ ^3P_2$
4647·32 (30)	21511·8	6s $^3P_0-6p^3D_1$	6s $^3P_0-6p\ ^3P_1$
4653·32 (8)	21484·1	6p $^3D_2-75$	6p $^3P_7-6d\ ^3P_1$
4711·26 (40)	21219·8	6s $^3P_0-6p\ ^1P_1$	Same
4735·44 (12)	21111·5	6s $^3P_1-6p\ ^3D_1$	6s $^3P_1-6p\ ^3P_1$
4757·81 (20)	21012·2	6p $^3D_2-73$	6p $^3P_2-6d\ ^1P_1$
4765·36 (20)	20978·9	6p $^3D_1-63$	6p $^3P_1-7s\ ^1P_1$
4802·01 (20)	20818·9	6s $^3P_1-6p\ ^1P_1$	Same
4832·82 (20)	20686·1	6p $^3D_2-71$	6p $^3P_2-6d\ ^3P_2$
4843·74 (10)	20639·5	6p $^3D_2-7s\ ^3P_2$	6p $^3P_2-7s\ ^3P_2$
4948·52 (3)	20202·5	6p $^3S_1-75$	6p $^3S_1-3d\ ^3P_1$
5021·68 (4)	19908·1	6p $^3D_2-63$	6p $^3P_2-7s\ ^1P_1$
5066·99 (2)	19730·1	$^3S_1-73$	$^3S_1-6d\ ^1P_1$
5152·30 (5)	19403·4	$^3S_1-71$	$^3S_1-\ \ ^3P_2$
5164·72 (6)	19356·8	$^3S_1-7s\ ^3P_2$	Same
5166·32 (12)	19350·8	$^1D_2-75$	$^1D_2-\ \ ^3P_1$
5176·55 (15)	19312·5	6s $^1P_1-6p\ ^1S_0$	Same
5381·20 (10)	18578·1	$^3P_2-^1D_2$	Same
5464·08 (15)	18296·3	$^3P_1-16$	$sp^3\ ^3D-6p\ ^3D_2$

TABLE V—(*continued*).

λ. I. A.	ν(vac).	Classification.	
		Lang.	Author.
5531·73(3)	18072·5	$37-6p^1S_0$	$sp^{33}P_1-6p^3D_2$
5555·99(1)	17993·6	$6p^1S_0-75$	$6p^1S_0-6d^3P_1$
5568·13(15)	17954·4	$6s^1P_1-6p^1D_2$	Same
5639·75(30)	17726·4	$6s^3P_2-6p^3S_1$	Same
5705·50(8)	17522·1	$6p^1S_0-73$	$6p^1S_0-6d^1P_1$
5825·50(5)	17161·2	$35-6p^1D_2$	$sp^{33}P_2-6p^1D_2$
5845·65(6)	17120·0	$6s^1P_1-{}^3S_1$	Same
5895·09(15)	16958·6	...	$6s^3P_0-6p^3D_1$
5981·42(1)	16713·8	$37-6p^1D_2$	$sp^{33}P_1-{}^1D_2$
6005·21(100)	16647·6	$33-40$	$6s^3P_1-{}^3D_2$
6079·79(30)	16443·3	$6s^3P_2-6p^3D_2$	${}^3P_2-{}^3P_2$
6130·04(50)	16308·6	${}^3P_2-{}^3D_3$	Same
6302·76(12)	15861·7	$37-{}^3S_1$	$sp^{33}P_1-{}^3S_1$
6319·76(5)	15819·0	$6s^1P_1-{}^3D_2$	$6s^1P_1-{}^3P_2$
6503·26(6)	15372·7	${}^3P_2-{}^3D_1$	${}^3P_2-{}^3P_1$
6546·86(1)	15270·3	$6p^3D_1-7s^3P_1$	$6p^3P_1-7s^3P_1$
6629·48(1)	15080·0	$6s^3P_2-6p^1P_1$	Same
6713·60(3)	14891·0	$35-{}^3D_3$	$sp^{33}P_2-6p^3D_3$
6778·75(2)	14749·5	$6s^1P_1-{}^3D_1$	$6s^1P_1-{}^3P_1$
6915·58(4)	14456·1	${}^1P_1-{}^1P_1$	$sp^{33}P_2-{}^3P_1$
7163·50(2)	13955·8	$35-{}^3D_1$	${}^3P_2-{}^3P_1$
7343·4	13613·0	$6p^1D_2-53$	$6p^1D_2-7s^1P_1$

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REFERENCES.

[1] S. G. Krishnamurty, *Proc. Roy. Soc.*, A, **151**, 178 (193[illegible]).
[2] Rao, *Proc. Lond. Phy. Soc.*, (in the course of publication).
[3] R. J. Lang and E. H. Vestine, *Phy. Rev.*, **42**, 233 (1932).
[4] *Cf.* 1 above.
[5] A. S. Rao, *Ind. Jour. Phys.*, **7**, 561 (1933).
[6] Tolansky, *Proc.. Roy. Soc.*, A, **146**, No. 856, 182 (1934).
[7] Badami, *Z. Physik.*, **79**, 206 (1932).
[8] Badami and K. R. Rao, *Proc. Roy. Soc.*, A, **140**, 387 (1933).