

ON THE SPECTRA OF DOUBLY IONIZED ARSENIC
ANTIMONY AND BISMUTH (As III, Sb III, Bi III)

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ABSTRACT

The spectra of the elements As III, Sb III and Bi III have been partially analyzed by the use of the irregular doublet law and the Moseley law and the published data for the two preceding elements of each iso-electronic sequence. In As III and Bi III the important terms from the configurations ns^2np , ns^2nd , $ns^2(n+1)s$ have been located and with the exception of the quartet P terms, those from the $nsnp^2$ configuration. (n is equal to 4 for As III, 5 for Sb III and 6 for Bi III.) In As III alone the 2P term of the np^3 configuration was found. The terms of Sb III located consist of some of those for the first three configurations only.

THE spectra of arsenic, antimony and bismuth should be very similar and since those of the two preceding elements in each iso-electric sequence have been partially analyzed it is possible to predict the doublet separations of the chief terms and the positions in the spectrum of some of the main line groups. References to the work of other investigators which has been used in this report are as follows: Ga I,¹ In I,¹ Tl I,¹ Ge II,² Sn II,³ Pb II.⁴

Most of the wave-length measurements recorded were made on a two-meter grating mounted in a vacuum spectrograph using the hot spark between metallic electrodes as source, but a few of the longer wave-lengths are taken from Kayser's Handbuch der Spektroskopie. The measurements for wave-lengths greater than 2000A are given in I.A. in air and for those less than this value in I.A. in vacuo.

The most important configurations of the iso-electronic sequences and the important terms arising from them in order of decreasing stability are as follows:

Configuration	Term	Configuration	Terms
n^*s^2np	2P	$ns np^2$	${}^4P {}^2D {}^2P {}^2S$
ns^2nd	2D	np^3	${}^2P {}^2D {}^4S$
$ns^2(n+1)s$	2S		

The first three rows on the left give the terms from the normal configuration (ns^2) of the next higher ion, the first row on the right gives the terms from the ($nsnp$) configuration of the ion and in the second row are recorded those terms to be expected from (np^2).

Tables I, II, and III give the term values and classified lines in As III, Sb III and Bi III respectively. The terms in each case are divided into

¹ Fowler, "Report on Series in Line Spectra."

² Lang, Proc. Nat. Acad. Sci. **14**, 32 (Jan., 1928).

³ Green and Loring, Phys. Rev. **30**, 5 (Nov., 1927).

⁴ Gieseler, Zeits. f. Physik **42**, 4 (1927).

* n has the value 4 for the first sequence, 5 for the second and 6 for the third.

odd and even and the configuration from which each arises is recorded. To save space, however, these configurations are not repeated in the designation of the lines in the first column of these tables. In order that it might be

TABLE I. Term values and classified lines in the spectrum of As III.

Designation	$\lambda(\text{\AA.})$	I	ν	$\Delta\nu$	Odd Terms		
					Config-uration	Term Values	
$bS-5P_1$	4226.87	6	23652	722	Config-uration	Term Values	
$bS-5P_2$	4101.49	6	24374				
$5S-5P_1$	4037.17	15	24763	723	$4s^24p$	$4P_1$	0
$5S-5P_2$	3922.61	20	25486			$4P_2$	2945
$5P_2-6S$	3255.69	8	30706	723	$4s^25p$	$5P_1$	131465
$5P_1-6S$	3180.78	5	31429			$5P_2$	132185
$5P_2-5D_2$	2989.54	2	33441	722	$4p^3$	cP_1	164284
$5P_2-5D_3$	2982.00	15	33525				
$5P_1-5D_2$	2926.32	10	34163				
bP_2-cP_2	2151.58	4	46461	2224	Even Terms		
bP_2-cP_1	2144.13	4	46624		Config-uration	Term Values	
bP_1-cP_2	2053.31	1	48685				
bP_1-cP_1	—	—	(48848)				
bD_2-5P_2	2133.89	1	46870	$4s^25s$		$5S$	106700
bD_3-5P_2	2147.59	5	46549		$4s^26s$	$6S$	162893
bD_2-5P_1	2166.28	2	46148			$4s^24d$	$4D_2$
bD_3-cP_2	1274.28	8	78476	$4D_3$	121168		
bD_2-cP_2	1268.97	5	78803	$4s^25d$	$5D_2$		165631
bD_2-cP_1	1266.39	30	78965		$5D_3$	165712	
$4P_2-bD_2$	1214.00	3	82372	2941	$4s\ 4p^2$	bD_2	85316
$4P_2-bD_3$	1209.28	15	82693			bD_3	85638
$4P_1-bD_2$	1172.15	12	85313			$4s\ 4p^2$	bP_1
$4P_2-5S$	963.75	20	103760	bP_2	117659		
$4P_1-5S$	937.20	20	106701	2945	$4s\ 4p^2$	bS	107814
$4P_2-bS$	953.57	20	104869				
$4P_1-bS$	927.52	20	107814	2948	$4s\ 4p^2$	bS	107814
$4P_2-bP_1$	888.98	20	112488				
$4P_2-bP_2$	871.73	25	114714				
$4P_1-bP_1$	866.28	15	115436				
$4P_1-bP_2$	849.91	15	117660	2939	$4s\ 4p^2$	bS	107814
$4P_2-4D_2$	849.34	1	117739				
$4P_2-4D_3$	845.86	2	118223				
$4P_1-4D_2$	828.65	2	120678	85	$4s\ 4p^2$	bS	107814
$4P_2-5D_2$	614.73	0	162673				
$4P_2-5D_3$	614.41	3	162758	2942	$4s\ 4p^2$	bS	107814
$4P_1-5D_2$	603.81	3	165615				

clear just which term is meant in any given case it was decided to use the total quantum number of the added electron for the terms arising from (ns^2) of the higher ion, while in the case of terms from the state ($nsnp$) of the ion the letter b is used and for the terms from (p^2) the letter c is used.

TABLE II. Term values and classified lines in the spectrum of Sb III.

Designation	λ (I.A.)	I	ν	$\Delta\nu$	Odd Terms		
					Config-uration	Term Value	
6S—6P ₂	4352.25	6u	22970	1668	5s ² 6p	6P ₁ 21302 6P ₂ 22970	
6S—6P ₁	4693.09	4u	21302				
6P ₂ —7S	3739.95	4u	26730.7	1669.3	Even Terms	Config-uration	Term Value
6P ₁ —7S	3520.11	1u	28400.0				
6P ₂ —6D ₂	3534.17	1	28287	237 1670	5s ² 6s 5s ² 7s	6S 0 7S 49702	
6P ₂ —6D ₃	3504.79	15	28524				
6P ₁ —6D ₂	3337.10	12	29957				
					5s ² 6d	6D ₂ 51259 6D ₃ 51496	

TABLE III. Term values and classified lines in the spectrum of Bi III.

Designation	λ (I.A.)	I	ν	$\Delta\nu$	Odd Terms		
					Config-uration	Term Value	
7P ₂ —7D ₂	3708.51	6	26957	710 5133	6s ² 6p	6P ₁ 0 6P ₂ 20373	
7P ₂ —7D ₃	3613.41	35	27667				
7P ₁ —7D ₂	3115.20	20	32091				
7S—7P ₂	3695.70	50	27051.9	5133.7	6s ² 7p	7P ₁ 112542 7P ₂ 117676	
7S—7P ₁	4561.33	40	21918.2				
6P ₂ —7S	1423.47	20	70251	20373	Even Terms	Config-uration	Term Values
6P ₁ —7S	1103.46	15	90624				
6P ₂ —6D ₂	1350.16	15	74065	1859 20374	6s ² 7d	7D ₂ 144634 7D ₃ 145344	
6P ₂ —6D ₃	1317.12	30	75924				
6P ₁ —6D ₂	1058.88	20	94439				
6P ₂ —bD ₂	1207.08	3	82845	1295 20373	6s 6p ²	bD ₂ 103218 bD ₃ 104513	
6P ₂ —bD ₃	1188.50	10	84140				
6P ₁ —bD ₂	968.82	10	103218				
6P ₂ —bS	989.87	12	101023	20373	6s 6p ²	bS 121396	
6P ₁ —bS	823.75	10	121396				

All the terms found are doublets; the doublet notation has been omitted for the sake of simplicity.

The results of the application of the irregular doublet law to the wave-number of the strongest lines in those multiplets which arise from inter-combinations of terms, the valence electrons for which have the same total quantum numbers, are shown in Table IV. It will be noted that for the

TABLE IV. *Position of corresponding lines by the irregular doublet law*

Line	Spectrum	ν	$\Delta\nu$	Line	Spectrum	ν	$\Delta\nu$
$4P_2-4D_3$	Ga I	33961	45281	$6P_2-6D_3$	Tl I	28407	26505
	Ge II	79242	38981		Pb II	54912	21012
	As III	118223			Bi III	75924	
$5P_2-5D_3$	Ga I	7749	13015	$7P_2-7D_3$	Tl I	6888	8348
	Ge II	20764	12761		Pb II	15236	12431
	As III	32525			Bi III	27667	
$5S-5P_2$	Ga I	8373	8590	$7S-7P_2$	Tl I	8683	9541
	Ge II	16963	8523		Pb II	18224	8828
	As III	25486			Bi III	27052	
$5P_2-5D_3$	In I	30703	37090				
	Sn II	67793					
	Sb III	—	—				
$6P_2-6D_3$	In I	6900	11069				
	Sn II	17969	10555				
	Sb III	28524					
$6S-6P_2$	In I	7775	7717				
	Sn II	15492	7478				
	Sb III	22970					

TABLE V. *Screening constants and differences by Sommerfeld formula.*

Term	Spectrum	$\Delta\nu$	σ_2	Δ	Term	Spectrum	$\Delta\nu$	σ_2	Δ
$4P$	Ga I	826	19.40	1.44	$6P$	Tl I	7793	53.43	3.40
	Ge II	1768	17.96	0.90		Pb II	14070	50.03	3.08
	As III	2943	17.06			Bi III	20373	47.95	
$5P$	Ga I	108	22.76	1.90	$7P$	Tl I	1001	62.47	5.46
	Ge II	360	20.86	1.11		Pb II	2813	58.01	3.89
	As III	722	19.75			Bi III	5134	54.12	
$4D$	Ga I	6	26.54	4.91	$6D$	Tl I	82.0	62.95	—
	Ge II	176	21.63	1.59		Pb II	—	—	—
	As III	484	20.04			Bi III	1859	57.80	
$5D$	Ga I	9	25.17	1.74	$7D$	Tl I	37.5	71.48	7.91
	Ge II	42	23.43	0.66		Pb II	29.9	63.97	3.32
	As III	85	22.77			Bi III	712	60.65	
$5P$	In I	2212	31.45	2.12					
	Sn II	4253	29.33	(1.70)					
	Sb III	(6960)	(27.62)						
$6P$	In I	292	36.86	2.86					
	Sn II	884	34.00	1.75					
	Sb III	1668	32.25						
$5D$	In I	23.5	36.66	3.63					
	Sn II	644	33.03	(4.00)					
	Sb III	(1815)	(29.00)						
$6D$	In I	50	40.05	2.52					
	Sn II	109	37.53	1.77					
	Sb III	237	35.86						

$nS-nP$ lines the doublet law holds very accurately in all the three sequences but in the case of the $nP-nD$ lines the differences Δ are quite irregular in the case of the lower quantum numbers (i.e., $4P_2-4D_3$ in the first sequence) while for the higher quantum numbers the results are quite uniform with the exception of the last sequence. As is stated below in connection with the screening constants it appears that the lines of the $6P-6D$ multiplet in Pb II may have been wrongly chosen. It should be stated here that the same failure of the irregular doublet law occurs for the $3P_2-3D_3$ lines in the sequence Al I, Si II, Pb III. That the failure is connected with the D terms may easily be seen by plotting $(\nu/R)^{1/2}$ against atomic number for these terms.

Table V gives a record of the screening constants for the doublet terms from the (ns^2) ion as calculated by Sommerfeld's formula

$$\Delta\nu = R\alpha^2(Z - \sigma_2)^4/n^3l(l+1)$$

THE CALCULATION OF TERM VALUES

The term values in this paper have been calculated by making the value of the lowest term for each element zero. This method was finally adopted because it was found impossible to arrive at any absolute value for the terms which was not open to serious objection.

TABLE VI.

	Terms	Diff.	Term Value	Relative Term Value	Value of Lowest Term ($4P_1$)
Ga I	5S		5S 24000	24788	48790
	6S	12797			
	$4P_1$		4P 49400	0	49400
	$6P_1$	40376			
	$7P_1$	3068	6P 8050	40375	48425
	$4D_2$	6021	4D 13370	34782	48150
	$5D_2$				
Ge II	5S		5S 67020	62402	129420
	6S	32378			
	$4P_1$		4P 134760	0	134760
	$5P_1$	79005			
	$4D_2$	19254	4D 45120	80834	125950
	$5D_2$				
As III	5S		5S 123642	106700	230340
	6S	56193			
	$4P_1$		4P 238275	0	238275
	$5P_1$	131465			
	$4D_2$	44947	4D 104382	120684	225070
	$5D_2$				

The usual method of arriving at absolute term values is by applying a Rydberg or Ritz formula to the wave-numbers of several measured lines which form a series converging to one limit. This method is well known to be very exact if a sufficient number of lines of one series can be measured but in these spectra, as in nearly all spectra of higher order, not more than two lines of any one series are known. To show that in such a case it is useless to attempt to calculate absolute term values with accuracy I have taken as an example these spectra of Ga I, Ge II and As III. In Table VI, column two gives the differences between the two terms of the same sequence, which of course is independent of any chosen values for these terms, column three gives the value of the lower of the two terms derived from these differences by the use of a simple Rydberg table, and column four shows the relative values of the terms based upon the lowest term given zero value. In the last column of the table are recorded the absolute values for the lowest term calculated by assuming the Rydberg formula to hold, first for the two *S* terms, then for the two *P* terms and lastly for the two *D* terms. In the case of Ga I the second *P* term is unknown and here the first and third *P* terms and also the third and fourth are used.

Table VI makes it clearly evident that the values of the lowest term ($4P_1$) arrived at by this method differ very largely depending upon whether the *S*, *P* or *D* terms are used in the calculation. In Ga I the $6P$ and $7P$ terms are known and from these we can arrive at a value for $4P_1$ which is probably nearest to the correct value. When this is done we see that in Ga I the first *P* terms give a value which is much too high and also the first two *S* terms give too large a value while the first two *D* terms give probably a somewhat low value but one which is likely to be nearer the correct value. We may perhaps conclude that the most probable value for the lowest term lies between those given by the first two *S* terms and the first two *D* terms and somewhat nearer the latter.

In Table VII the most probable values for the lowest terms of the three elements of the iso-electronic sequence are given as arrived at in this way together with an estimation of the error in each and a value for the ionization

TABLE VII. *Most probable values of lowest terms and ionization potentials.*

Spectrum	Lowest term value (cm^{-1})	Ionization potential, (volts)
Ga I	48350 ± 50	5.97 ± 0.07
Ge II	127000 ± 500	15.6 ± 0.1
As III	226500 ± 1500	28.0 ± 0.2
Bi III	210000 ± 2000	25.9 ± 0.3

potential in volts. In the table will also be found an estimate of the lowest term P_1 of Bi III by means of the same method but since the $5P$ term of Sb III is still unknown no estimate has been made here but $6S$ has been made equal to zero.

Another method which has been suggested for arriving at the approximate values for the terms when few terms are known is to make the Rydberg denominators for the first S terms in an iso-electronic sequence increase by equal amounts. This method when applied to the case in hand gives about the same values for the lowest terms as were arrived at by the method outlined above. Here one must, however, assume that the term values for at least one element in the sequence are known with sufficient accuracy so that usually one cannot arrive by this method at very accurate values for the terms. Even in cases where several terms of the same series are known with fair accuracy as is the case in Ga I still a sequence of S terms gives a value considerably larger than a sequence of D terms.

A brief discussion of each of the spectra investigated will now be given.

SPECTRUM OF AS III

This spectrum seems quite regular as shown in Tables IV, V and VI with the possible exception of the nD terms. It will be found that this irregularity is a prominent feature of all of the D terms in all three sequences. It is to be expected also that the lines of this multiplet would appear with much more intensity than those recorded in Table I.

The cP terms are doubtful and in connection with the combination of these terms with bD and bP a peculiar situation was found which may be worth recording. Besides the intercombination of cP with each of these two terms bD and bP which have been recorded in Table I, three lines were found which agree within experimental error with the values expected for an intercombination between the bD and bP terms themselves. It will be seen that not only are the values rather accurate but the intensity rules are obeyed as well.

	λ	I	ν (obs)	ν (cal)
$bD_2 - bP_1$	3319.25	(1)	30119	30119
$bD_3 - bP_2$	3122.06	(4)	32020	32021
$bD_2 - bP_2$	3091.18	(3)	32340	32343

The wave-lengths were taken from Kayser's Handbuch der Spektroskopie, Vol. V, and occur in the spectrum from a Geissler tube in which it appears the spectral lines of these doubly-ionized atoms frequently occur. The occurrence of these lines with wave-lengths so accurately of the predicted value may be accidental or it may mean that one of these terms should be really an odd term and that then one of the combinations with cP is unreal.

The author is greatly indebted to Dr. R. A. Sawyer for his kindness in putting the wave-length measurements of arsenic made on the vacuum spectrograph at the University of Michigan at his disposal and also for pointing out to him the significance of the strong doublet at $\lambda 953A$.

SPECTRUM OF SB III

Two pairs of lines which evidently belong to this spectrum have been already given,⁵ the less refrangible pair of which has been classified here as

⁵ Nayaran and Rao, Nature, **120**, (July, 1927).

6*S*–6*P* while the other falls at 4590 and 4265A. Several further pairs having this 6*P* separation have now been located including the other two listed in Table II. One of those not yet classified lies in the far infra-red⁶ at 12118.9 and 10079.9A and several pairs were found in the far ultra-violet. Professor Green has very kindly taken the Zeeman pattern of the lines of the three groups of Table II and finds qualitative agreement with the classification there given except for the first group which does not seem to show quite the characteristics of a Principal pair. The same, however, may be said for the other pair at 4590 and 4265A but it would seem that these constitute about the only choice for this Principal doublet and so the pair shown in Table II has been tentatively assigned to 6*S*–6*P* until further information can be obtained.

The 5*P* terms of this spectrum could not be located with any degree of certainty. It was found that a value of $\Delta\nu = 8100$, approximately, occurs quite frequently and it is easy to build up a plausible scheme on this basis but such a value seems much too large for the 5*P* separation as compared with In I and Sn II. Until this doublet term can be located it is not possible to proceed to the terms of the (*sp*²) configuration. It may be stated that in the spectrum of the hot spark between 600 and 1200A there are some sixty lines with intensities ranging from (10) to (50) and it would seem certain that before very much progress can be made in the analysis of these complex spectra some means must be devised which will separate the lines in the extreme ultra-violet into classes corresponding more or less closely to the various stages of ionization of the atom. Such a method will of course need to be adapted to elements which exist normally in the solid state.

SPECTRUM OF Bi III

This spectrum probably cannot be classified in a completely satisfactory manner until certain further information is available concerning the spectrum of Pb II. The reality of the two levels classified as 6*D*₂ and 6*D*₃ in Pb II appears to be well established but it would be indeed surprising to find in this one-electron spectrum an inverted doublet with a separation of 776 cm⁻¹. The two configurations (6*s*6*p*²) and (6*s*²6*d*) are expected to give rise altogether to four levels with *j* = 2 lying in the same neighborhood. Three of these have been found; it appears quite possible that the missing one is 6*D*₂.

On the other hand it is quite possible on the basis of separations and intensity relations alone to find a possible multiplet in Bi III which could arise from inverted *D* terms simply by substituting the line 1394.05(20)71733 for the line 1317.12(30)75924 in the multiplet given in Table III.

In regard to 7*P*–7*D* it seems probable that the faint multiplet in Pb II has been classified incorrectly since the 7*D* term so obtained does not give a 6*P*–7*D* multiplet in the author's table of wave-lengths of the ultra-violet. There is a group of lines in the spectrum of Pb which may possibly be 6*P*–7*D* as follows:

⁶ Randall, *Astrophys. J.* **34**, (July, 1911).

λ	I	ν
1279.44	15	78159
1274.56	10	78458
1080.84	2	92521

Of course this group is open to the same criticism which was made of $6P-6D$ above.

In conclusion the author wishes to convey to Dr. Goudsmit and to Dr. Mack of the University of Michigan his sincere thanks for very helpful criticisms in connection with the writing of this report and to express to the Research Council of Canada his appreciation of a grant for carrying on this research.

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