

A REGULARITY OBSERVED IN THE SECOND SPARK SPECTRUM OF IODINE.

BY J. B. SETH, M.A. (Cantab.),
Professor of Physics, Government College, Lahore.

Received February 15, 1935.

SPECTRA of most elements have by now been elucidated more or less fully. Iodine is one of the few left, the lines of which still remain mainly unidentified except for just a few regularities observed, an account of which only has so far been published.¹ An attempt to classify the lines attributed to the second spark spectrum of Iodine (I^{++} or I III) was started by the present author sometime ago and an account is given here of the progress made so far.

The atomic number of Iodine being 53, the structure of its extra-nuclear electrons is given by the following scheme² (Chart 1).

No. of level	Name of level with the number of electrons in it
1	K_1 2
2	L_1 L_2 2 6
3	M_1 M_2 M_3 2 6 10
4	N_1 N_2 N_3 N_4 2 6 10
5	O_1 O_2 O_3 O_4 2 5
6	P_1 P_2 Etc.

CHART 1.

The number of electrons left in doubly ionised Iodine is 51. The last line in the above scheme thus modifies to the following (Chart 2) in case of I^{++} .

5	s O ₁ 2 ¹	p O ₂ 2+(1)	d O ₃	f O ₄
---	---------------------------------------	------------------------------	---------------------	---------------------

CHART 2.

The various normal spectral terms will generally be given by the successive "jumps" of the last electron, put within brackets in the above scheme, from one level to the next. The kind of terms expected in the various levels is given below (Chart 3). These terms are obtained by the application of rules developed by Russel, Pauli, Heisenberg and Hund. A complete list of terms due to similar electrons has been given by Gibbs, Wilber and White.³ The method of calculating the terms expected in any actual case as the running electron moves from level to level can be easily understood from a paper by Saha⁴ in which he has made the calculation for spectral terms of Alkaline Earths.

Electronic Configuration	Nomenclature	Expected terms
2O ₂ . O ₂	5p	⁴ S, ² (PD).
2O ₂ . O ₃	5d	} ⁴ (FDP), ² (GFDPS).
2O ₂ . P ₃	6d	
2O ₂ . Q ₃	7d	
Etc.	Etc.	
2O ₂ . P ₁	6s	} ⁴ P, ² (DPS).
2O ₂ . Q ₁	7s	
Etc.	Etc.	
2O ₂ . P ₂	6p	} ⁴ (DPS), ² (FDPS).
2O ₂ . Q ₂	7p	
Etc.	Etc.	
2O ₂ . O ₄	5f	} ⁴ (GFD), ² (HGFDPS).
2O ₂ . P ₄	6f	
2O ₂ . Q ₄	7f	
Etc.	Etc.	

CHART 3.

A very exhaustive list of wavelengths of lines belonging to the first second and third spark spectra (E₁, E₂, E₃) of Iodine had been published by Mm. L. and E. Bloch⁵ shortly before the present work was taken in hand. A reprint of this paper had been sent by the authors to Dr. P. K. Kichlu of

this laboratory, who kindly put it in my hands and to whom I am deeply indebted for the present work. The reason for selecting I^{++} instead of I^+ was the smaller, and therefore more manageable, number of lines attributed to the former and the existence of previous data which could give clue to the identification of these lines, namely, the elucidation of the various spectra of F, Cl and Br by Dingle,⁶ Bowen⁷ and Deb⁸ respectively, also the spectra of In^{++} , Sn^{++} and Sb^{++} by Rao (K. R.)⁹, Green and Loring¹⁰ and Pattabhiramiah and Rao (A. S.)¹¹ respectively. The number of lines classified under the third spark spectrum (E_3) of Iodine is much smaller in Blochs' list than that under E_2 and, therefore, more manageable and might have been selected for elucidation. But not much data existed to give a clue to this spectrum.

From the term values given by the above-mentioned authors for the various levels of In^{++} , Sn^{++} and Sb^{++} , it was sought to get an idea of the wave-number of the lines in the multiplet due to the transition $P_1 \rightarrow P_2$ or $6s-6p$ for I^{++} as indicated in Table I.

TABLE I.

Level	Term value for level				
	In^{++}	Sn^{++}	Sb^{++}	Te^{++}	I^{++}
	calculated from observations				extra- polated
6s	101,051	103,604	107,456	..	
6p (Lowest)	82,003	81,802	84,016	..	
6s—6p	19,048	21,802	23,440	..	25,600
Atomic no. of the element	49	50	51	52	53

The plot between 49, 50, 51 for numbers 19,000, 21,800, 23,400 respectively gives the graph given in Fig. 1, from which the corresponding number for 53 comes out to be about 25,600.

This is an unorthodox method for finding the order of the wave-number to be attributed to any particular transition. But from the absence of any data, available at the time, by means of which this could be done in the usual manner, the present device had to be resorted to. Saha's

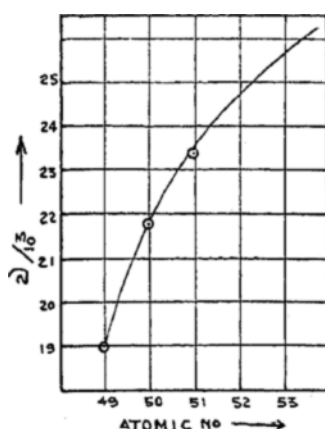


FIG. 1.

horizontal rule¹² could not be applied as the spectrum of Te^+ had not been elucidated till then. Since then this has been done by Deb and Mohanti¹³ and an inspection of this paper indicates that the lines for the above transition should be expected in the region obtained above, namely ν 25,600. It must be mentioned, however, that a scrutiny of the last-mentioned paper shows that there are some serious discrepancies in the list of identification of lines given in it.

In Blochs' list for I^{++} , there is a strong line occurring at λ 3940, ν 25374, of which the intensity given is 10. This is the highest number for intensity given by the Blochs to the E_2 lines of Iodine. In the region of ν 24000-26000, also appear in their list quite a number of strong lines with intensities 8, 7, 5, etc., the above-mentioned line 25374 being the strongest in this region. It was, therefore, natural to regard this line as belonging to the 6s-6p multiplet.

Once again, an unorthodox method was used to get a clue to the differences between the various inner quantum levels of 6s ^4P and 6p ^4D by extrapolating from the corresponding differences observed in the second spark spectra of F, Cl and Br. The plots between the atomic numbers of these three elements and the various sub-level differences are given in Fig. 2, from which the corresponding differences for Iodine come out to be about 610 for $\text{P}_1\text{-P}_2$ and 1100 for $\text{P}_2\text{-P}_3$ in the 6s ^4P level and 360, 680 and 850 respectively for $\text{D}_1\text{-D}_2$, $\text{D}_2\text{-D}_3$ and $\text{D}_3\text{-D}_4$ in the 6p ^4D level.

Armed with these conclusions it was found possible to build up a multiplet for the 6s-6p quartet combination by putting the line 25374 at $6s\ ^4\text{P}_3 \rightarrow 6p\ ^4\text{P}_3$ where a fairly strong (though not the strongest) line may be expected from considerations of intensity rules. The differences $\text{P}_1\text{-P}_2$, $\text{P}_2\text{-P}_3$, $\text{D}_1\text{-D}_2$, $\text{D}_2\text{-D}_3$, $\text{D}_3\text{-D}_4$ turned out to be 576, 1090, 320, 625 and 835

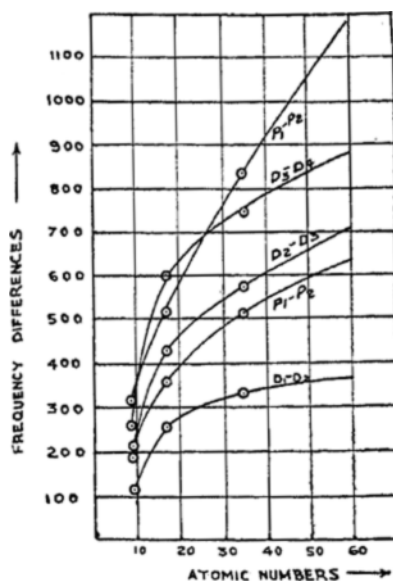


FIG. 2.

respectively and a preliminary announcement about the results obtained was made in *Nature*.¹⁴ Further work on these lines, however, did not lead to any reliable and complete elucidation of the spectrum, although by putting the line 25374 at $6s \ ^4P_3 \rightarrow 6p \ ^4D_4$, where a really strong line is expected and using frequency differences slightly different from those given above, lines could be found and about 120 of them "pieced together" so as to apparently account for as many number of lines for the quartet combinations between 6p and the four surrounding levels, 6s, 6d, 5d and 7s. But from the fact that the differences between two horizontal rows and those between two vertical columns in the multiplets pieced together differed from each other by several units of wave-numbers, the highest divergence between the maximum and minimum values of the differences in any set being 10 and the mean divergence for 23 sets being 6, no reliance could be put on the conclusions reached. This piecing together of multiplets was really based on the published work⁸ for Br^{++} in which also the measurements by the Blochs were used. This paper on Bromine identifies 156 lines of Br^{++} spectrum but an analysis of the multiplets given also shows sometimes quite large divergences between the maximum and minimum values of the differences occurring between rows or between columns. Thus of the 30 sets of such differences that the present author calculated the largest divergences come out to be 14 while the mean divergence from these 30 sets is 6. These large discrepancies have been remarked upon by other workers as well.¹⁵

In the classification for Te^+ mentioned above¹³ the lines were also taken from Blochs' list. In this identification, disregarding other discrepancies, as far as the divergences between inner quantum level differences are concerned, the largest divergence is 8 and the mean, 4, from 19 sets of differences that were calculated by the present author. Since all these rather unsatisfactory identifications are based on Blochs' measurements, it was felt that using these, one may not get as good an agreement between the various differences as one finds to exist in, for instance, chlorine and fluorine spectra and as, one feels, ought to exist in a correct classification. Another worker, Asagoe¹⁶ of Japan, has also made measurements on the lines of the halogen elements and classified them under various degrees of excitation. I am indebted to him for sending me a copy of the reprint of his paper. But the accuracy of measurements attained seems to be even less than that of the Blochs. During this time, however, had come to hand a paper by Kerris¹⁷ from the Physical Institute of the University of Bonn, giving a fairly large number of lines in the spectrum of Iodine (though not as numerous as in Blochs' list) which, from the fact that some wavelengths are given to seven significant figures and all the wave-numbers also to seven figures, one felt must be very accurate. Kerris did not classify the lines for the various degrees of excitation but making use of the classification into E_1 , E_2 , E_3 by the Blochs and into II, III, IV by Asagoe, out of all the 531 lines measured by Kerris, all those were sorted out which belonged to or had any likelihood of belonging to the spectrum of doubly ionised iodine, *i.e.*, all those that were marked as E_2 in Blochs' list and also III in Asagoe's list (2, III) (123 lines); all those that were marked as E_2 by the Blochs but did not occur in Asagoe's list (2) (number of lines, 40); similarly (III) (6); (2, III?) (5); (2,—) (1) meaning a line classified by B as E_2 but left unclassified by A; (2?) (1); (III?) (2); (2, II?) (2); (2, II) (11); (1, III) (8); (2, IV) (2); (3, III) (1); (1, III?) (2); (II?) (6); (1, II?) (5); (1,—) (3); (3,—) (1) and finally six lines which occur in A's list but not in B's but which were not classified by A and also 49 lines which are found in K's list but not in A's or B's.

The total number of lines so obtained was 274 and by bitter past experience it was felt that the only way in which any trustworthy regularities could be isolated was to find out all the possible differences between all the lines. Confining these differences up to within a maximum difference of about 15,500, this required performing about 35,000 subtractions, each subtraction being done on one separate slip of paper, arranging them in serial order and finding from them groups in which the differences are almost identical. In this manner the following 17 groups (Table II) were

TABLE II.

Frequency difference	Wave-number pairs giving this frequency difference.						
131.2 } .3 }	19737.1 19605.9	30945.4 30814.1	34394.4 34263.2	35239.1 35107.9	35707.9 35576.6	35839.1 35707.9	
146.8 } .9 }	17695.6 17548.7	18494.7 18347.9	24334.2 24187.3	25372.0 25225.1	26161.3 26014.5	32482.9 32336.1	
515.8 } .9 }	19989.1 18473.3	23061.4 22545.5	24187.3 23671.4	24685.1 24169.2	25309.9 24794.0	26309.6 25793.7	
799.1 } .2 }	18347.9 17548.7	18494.7 17695.6	21933.3 21134.1	25357.7 24558.6	31664.7 30865.6	32902.9 32103.8	
2280.7 } .8 }	21828.0 19547.2	24214.0 21933.3	26839.4 24558.6	27118.0 24837.3	29840.1 27559.4	33568.4 31287.6	
2380.9 } 1.0 }	18810.9 16429.9	26715.2 24334.2	28460.0 26079.1	30814.1 28433.1	31664.7 29883.7	35249.0 32908.1	
2625.3 } .4 } .5 }	21436.3 18810.9	24558.6 21933.3	26839.4 24214.0	27899.1 25273.7	29561.5 26936.1	30524.5 27899.1	35105.5 32480.0
2904.0 } .1 }	21715.0 18810.9	24837.3 21933.3	27118.0 24214.0	29840.1 26936.1	29908.6 27004.6	32958.1 30054.0	
3160.3 } .4 }	18282.6 15122.2	22798.3 19637.9	25093.7 21933.3	25651.8 22491.4	28712.3 25552.0	30266.1 27105.7	
3209.6 } .7 }	19850.8 16641.2	21874.6 18664.9	24645.9 21436.3	26252.6 23042.9	27768.3 24558.6	31108.7 27899.1	32771.1 29561.5
3307.2 } .3 }	18499.5 15192.3	18830.2 15523.0	19737.1 16429.9	23042.9 19735.6	29561.5 26254.2	32209.9 29595.6	
4446.3 } .4 }	24214.0 19767.6	26161.3 21715.0	27004.6 22558.2	29283.7 24837.3	30098.1 25651.8	34848.0 30401.6	
5504.9 } 5.0 }	24769.6 19264.7	25499.0 19994.0	29176.4 23671.4	30342.2 24837.3	30896.4 25391.4	34681.3 29176.4	
5669.3 } .4 }	22310.5 16641.2	24334.2 18664.9	27105.7 21436.3	28712.3 23042.9	29142.8 23473.5	33568.4 27899.1	
6462.7 } .8 }	24794.9 18332.2	25273.7 18810.9	27899.1 21436.3	31108.7 24645.9	33568.4 27105.7	38956.6 32492.8	
7350.3 } .4 }	23473.5 16123.1	24769.6 17419.2	26161.3 18810.9	27118.0 19767.6	29283.7 21933.3	29908.6 22558.2	33659.9 26309.6
11061.9 } 2.0 }	26252.6 15190.7	26254.2 15192.3	29561.5 18499.5	29622.4 18560.4	35231.1 24169.2	35707.9 24645.9	

found such that each consisted of at least 6 differences within 0.1 of each other. The wave-numbers, etc., have for this purpose (and for later work) been rounded off to one place of decimals from Kerris's two, although when performing the subtractions both places of decimals were used. It may

TABLE III.

Rows ↓	Columns →	1	2	3	4	5	6	7	8	9	10
	Provisional Term assignment → ↓	$6p\ ^4D_1$	$6p\ ^4D_2$	$6p\ ^4P_1$	$6p\ ^4P_2$	$6p\ ^4P_3$	$6p\ ^4S_2$	$6p\ ^2F_3$	$6p\ ^2D_2$	$6p\ ^2P_2$	Z_2 or s
1	$5d\ X_1$			(1) 32492.8	(3) 34099.6				(10) 38955.6		
2	$6s\ ^4P_1$	(2) 22310.5	(4) 24334.2	(10) 27105.7	(5) 28712.3				(2) 33568.4	(00) 35231.1	
3	$6s\ ^4P_2$	(4) 19850.8	(6) 21874.6	(2) 24645.9	(10) 26252.6	(2) 27763.3			(0) 31108.7	(1) 32771.1	
4	$6s\ ^4P_3$			(4) 22078.2	(8) 23684.6	(14) 25431.6	(15) 25651.8	(3) 27712.1			
5	$6s\ ^2D_2$		(4) 19306.6					(3) 27481.1			(6) 30271.6
6	$6s\ ^2D_3$			(0) 21715.0	(4) 24837.3			(8) 27118.0		(3) 29840.1	(3) 29908.6
7	$6s\ ^2P_2$	(00) 16641.2	(2) 18664.9	(2) 21436.3	(0) 23042.9	(8) 24558.6		(10) 26839.4	(6) 27899.1	(2) 29561.5	
8	$6s\ ^2S_1$	(00) 15232.9			(1) 21635.0				(3) 26491.3		
9	$5d\ ^2P_2$ (?)		(00) 16039.3	(2) 18810.9	(3) 21933.3	(3) 21933.3	(2) 22153.8	(5) 24214.0	(0) 25273.7	(4) 26936.1	(2) 27004.6
10	$5d\ Y_2$				(4) 19547.2		(2) 19767.6	(3) 21828.0			

also be remarked here that the four differences (also within 0.10 of each other) given by Kerris himself have no real significance, for they are between wave-numbers which do not necessarily belong to the spectrum for the same degree of excitation.

With these groups as a starting point, finding all the inter-differences between corresponding lines belonging to each group, searching for similar other differences amongst all the 35,000 differences mentioned above and then co-ordinating together all the suitable and intercombining lines, from amongst all those found by the above process, the regularity given here (Table III) stood out. This includes 51 lines. The intensity of each line as determined by Kerris is given within brackets above each wave-number. The highest figure for intensity given by Kerris is 15.

It is felt that such a regularity cannot be merely fortuitous but must be real. A proper and full attempt to place these lines so as to form a possible multiplet in the spectrum of I^{++} and building this up so as to be able to identify as many of the remaining lines as possible has not yet been made. But a rough preliminary attempt at simply placing the lines of Table III showed that if columns and rows in it are marked as shown in the Table then, except for one line, ν 21715 (col. 3, row 6) shown enclosed in the Table the other numbers fall at places where a line may be expected. The intensity rules for lines are also generally satisfied. The differences between various columns and rows come out as given in Table IV in which each set of differences is headed by the serial number and the numbers of columns or rows of which they are the differences and is followed by the number of differences in each set and the divergence between the highest and lowest figure of the group.

The total number of sets in Table IV are 35, the total number of differences composing these sets being 136. It is easily seen that the divergences between maximum and minimum differences belonging to any one set are remarkably small, nowhere being more than 0.5, while the average of all such divergences comes out to be 0.2. It may be interesting to mention here that using the values of wave-numbers calculated from the wave-lengths given in Blochs' list in place of Kerris's numbers in Table III, and calculating the various differences after the manner of Table IV, the mean divergence was found to be 1.3 while the maximum divergence was 5.6. From the Tables III and IV, it is easy to calculate the relative values for the various terms involved. These are given in Table V. The identification of the various azimuth quantum numbers (S, P, D, etc.) may prove to be incorrect but the relative term values and the inner quantum numbers should be correct.

TABLE IV.

Differences between Columns			Differences between Rows		
1. 1 & 2	8. 8 & 9	14. 3 & 8	19. 1 & 2	25. 9 & 10	31. 4 & 10
2023.7	1862.7	6462.8	5387.1	2386.1	5884.4
.8	.4	.7	.3	.2	.2
.7	.4	.8	.2	.0	.1
(3) 0.1	(4) 0.3	(5) 0.1	(3) 0.2	(3) 0.2	(3) 0.3
2. 2 & 3	9. 9 & 10	15. 3 & 9	20. 2 & 3	26. 3 & 6	32. 5 & 7
2771.5	68.5	8125.4	2459.7	2930.9	641.7
.3	.5	.2	59.6	1.0	.9
.6	(2) 0.0	.1	59.8	1.0	.7
.4	10. 1 & 8	.2	59.7	(3) 0.1	.7
.6	11257.9	(5) 0.3	59.7	27. 3 & 7	(4) 0.2
(5) 0.3	7.9	16. 3 & 10	60.0	3209.8	33. 5 & 9
3. 3 & 4	7.9	(5) 0.3	(6) 0.4	.7	3287.3
1806.8	8.4	8193.4	21. 3 & 5	.6	.3
.6	(4) 0.5	.6	2568.0	.7	.1
.7	11. 2 & 8	.7	7.7	.7	.0
.4	9234.2	(3) 0.3	8.0	.6	(4) 0.3
.6	.1	17. 4 & 8	(3) 0.3	.6	34. 6 & 9
(5) 0.4	.2	4856.0	(7) 0.1	.4	2904.1
4. 4 & 5	.4	.1	22. 5 & 6	28. 3 & 8	.0
1515.7	(4) 0.3	.1	363.2	4617.9	.0
.7	12. 3 & 5	.2	.1	.6	.0
(2) 0.0	3122.4	.3	.0	.4	.0
5. 5 & 6	.3	(5) 0.3	(3) 0.2	(3) 0.5	(5) 0.1
220.2	.3	18. 5 & 7	23. 6 & 7	29. 3 & 9	35. 7 & 9
.5	.4	2280.5	278.7	5835.3	2625.6
.4	(4) 0.1	.7	.7	.0	.4
(3) 0.3	13. 3 & 7	.8	.6	.0	.3
6. 6 & 7	5402.9	.7	.6	.0	.4
2060.3	3.0	.8	(4) 0.1	(3) 0.5	.4
.2	3.1	(5) 0.3	24. 7 & 8	(5) 0.3	(6) 0.3
.4	3.1	1408.3	1408.3	30. 4 & 9	
(3) 0.2	(4) 0.2	7.9	7.9	3498.3	
7. 7 & 8		7.8	7.8	.0	
1059.7		(5) 0.3	(3) 0.5	.1	
.7				(3) 0.3	
(2) 0.0					

TABLE V.

Term	Term value	Term	Term value	Term	Term value
6p Z_2	0	6p 4P_1	8193.7	6s 4P_3	30503.0
6p 2P_2	68.5	6p 4D_2	10965.2	6s 4P_2	32839.7
6p 2D_2	1731.0	6p 4D_1	12988.9	6s 4P_1	35299.4
6p 2F_3	2790.7	6s 2S_1	28222.3	5d Y_2	24618.6
6p 4S_2	4851.0	6s 2P_2	29630.3	5d $^2P_2(?)$	27004.7
6p 4P_3	5071.4	6s 2D_3	29908.9	5d X_1	40686.6
6p 4P_2	6587.1	6s 2D_2	30272.0		

It may be mentioned in the end that the total number of lines ascribed by the Blochs definitely to E_2 of Iodine is 531 whereas 63 more might also belong to this spectrum having been classified in Blochs' list as $E_1 ?$ (25), $E_2 ?$ (23) or $E_3 ?$ (15). Corresponding numbers for lines given by Asagoe were 223 and 76. Of the 51 lines of Table III, 35 belong to the (2, III) category, 9 to (2), 2 to (2, II), one each to (2, -), (II ?), (1, II ?), and (3, III) and one line which is in K list but not in A or B.

In view of Table IV, it seems almost certain that the regularity of Table III is a genuine one. It is hoped that after further scrutiny and work, the identification of terms ascribed to the rows and columns of Table III will prove to be correct and that at any rate it will lead to a complete analysis of the spectrum of doubly ionised iodine.

REFERENCES.

1. Turner, *Phys. Rev.*, 1926, 27, 396.
Evans, *P.R.S.*, 1931, A 133, 417.
Deb, *P.R.S.*, 1933, A 139, 380.
2. Saha, *Phil. Mag.*, June 1927, the chart facing p. 1273.
3. *Phys. Rev.*, Jan. 1927, 790-793.
4. *Phil. Mag.*, June 1927, 1269-70.
5. *Ann. de Physique*, 1929, 11, 141-166.
6. *P.R.S.*, 1929, A 122, 144.
7. *Phys. Rev.*, 1928, 31, 34.
8. *P.R.S.*, 1930, A 127, 197.
9. *Proc. Lond. Phys. Soc.*, 39, 153.
10. *Phys. Rev.*, 30, 586.

11. *Ind. Jour. Phys.*, **3**, 443.
12. *Ind. Jour. Phys.*, **3**, 67-76.
13. *Bulletin of the Academy of Sciences of U.P. (India)*, **1**, 38.
14. *Nature*, Jan. 31, 1931, **127**, 165.
15. *Atomic Energy States* by Bacher and Goudsmit, p. 97.
16. *Memoirs of the College of Sciences, Kyoto Imperial University*,
Series A, **12**, 275.
17. *Zeits. f. Phys.*, 1930, **60**, 20.