INVESTIGATIONS ON THE SPECTRUM OF BROMINE PART II—STRUCTURE OF Br II

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ABSTRACT. The analysis of the spectrum of Br. II, reported by Bloch and Lacroute has been confirmed by a close examination of the individual lines forming the various triplet groups. With the aid of some of the known terms, the fundamental triplet giving the ground term $^4p\ ^3p$ has been identified in the vacuum grating region. The analysis is extended to include new terms, chiefly of the 5d configuration, based on the ^2D state of the ion. Altogether about hundred lines have been newly classified, thirty of which are lying below λ 1100.

INTRODUCTION

In Part I of these investigations (Rao and Krishnamurty, 1937) the structure of the spectrum of doubly ionised Bromine (Br III) was described and the energy values of some of the doublet and quartet terms of the spectrum were determined. This part is devoted to the elucidation of the structure of the singly ionised atom (Br II), which is as yet not known completely.

The previously published work on the analysis of Br II comprises mainly of two different investigations, one by S. C. Deb (1930) and the other by Bloch and Lacroute (1931 and 1934). The conclusions arrived at by Deb are found to be entirely erroneous and will not be considered here. Bloch and Lacroute (1931) were the first to locate the prominent quintuplet groups in the visible region. In later work (1934) they reported the identification of 45 terms of Br. II based on the ^4S and ^2D states of Br III. Some of these identifications were confirmed by a study of the Zeeman effect of 26 lines of Br II. Still, many of the characteristic terms of Br II, which are to be predicted on Hund's theory and shown in Table I, have remained unidentified, the most important of these being the ground terms ^3P, ^1D, ^1S, of the deepest 4p configuration.

TABLE I

Predicted terms of Br II

Electron configuration	Terms Limit ^4S		^2D	^2P
$4s^24p^4$		^3P	^1D	^1S
$4s^24p^3\ 5s$	^5S	^3S	^3D ^1D	^3P ^1P
$4s^24p^3\ 5p$	^5P	^3P	^3F ^3D ^3P ^1F ^1D ^1P	$^3D^3P^3S$ $^1D^1P^1S$
$4s^24p^3\ 4d$	^5D	^3D	^3G ^3F ^3D ^3P ^3S ^1G ^1F ^1D ^1P ^1S	$^3F^3D^3P$ $^1F^1D^1P$
$4s^24p^3\ 5d$	^5D	^3D	^3G ^3F ^3D ^3P ^3S ^1G ^1F ^1D ^1P ^1S	$^3F^3D^3P$ $^1F^1D^1P$
$4s^24p^3\ 6s$	^5S	^3S	^3D ^1D	^3P ^1P

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In the present paper an extension of the analysis is made and terms of the 4p and 5d (^{2}D) configurations are determined.

The main experimental work forming the basis of this investigation was already described in Part I. In addition, an examination is made of the feeble spark spectra between graphite poles containing various bromides and discharges through the vapours of bromides excited by a small induction coil, with a view mainly to identifying the groups of lines which have similar behaviour and appearance—under different conditions of excitation. These observations helped in allocating lines to the same multiplet, *e.g.* (^{3}D→^{3}F) or (^{3}F→^{3}G) etc. without depending merely on the equality of wave number intervals which sometimes might be accidental.

ANALYSIS

A close scrutiny of the plates, in the manner described above, has enabled the authors first of all to confirm the identification of 5s ^{5}S, ^{3}S and 5p ^{5}P, ^{3}P and the group of terms of the 5p configuration based on ^{2}D state of the ion, made previously by Bloch and Lacroute. With the help of these terms and the combinations which they are expected to form in the vacuum grating region, the terms 4 p ^{1}P ^{1}D and 5s ^{3}P ^{1}P have been detected. The chief triplet 4p ^{3}P-5s ^{3}S is identified, leading to further classifications which are shown in Table 2*a*. The 5s ^{1}D term determined by Bloch and Lacroute as 65657.1 has been altered to 61179.5, the intensities of the combinations supporting the alteration.

All the 5p terms shown in Table 2 are due to Bloch and Lacroute with the exception of 5p ^{3}F$_4$ which is newly determined. The ^{5}D terms identified by Bloch and Lacroute are here assigned to the 5d instead of to the 4d state, as the latter are expected to be deeper than the 4d ^{3}D term and of the same order of magnitude as the 5s (^{4}S) terms. A comparison of the relative values of 4d and 5s terms in Se I., Br II and Kr III indicates that a crossing of the curves takes place at the third stage in Kr III. The combinations between 5d ^{5}D and the 5p terms shown in Table 2(*a*) and due to Bloch and Lacroute. They have expressed a doubt as to the correctness of the components ^{5}D$_0$ and ^{5}D$_1$. The level ^{5}D$_0$ depends on the assignments of the single line 25540.8. The behaviour and appearance of the lines are not inconsistent with Lacroute's classification which is here adopted. The 5d ^{3}D assignments are due to the authors. Table 2(*b*) contains multiplets involving the 5d (^{2}D) terms. Only four of these are due to Bloch and Lacroute. The rest are new. The 6*s* (^{2}D) terms are also shown in the same table but their identification is incomplete and perhaps uncertain. The level ^{3}D$_1$ gives nine combination lines of which three are otherwise classified.

In addition to the terms shown in Table 2 Bloch and Lecroute have also mentioned the following terms:—77679·6, 75311.6—65657·1$_1$ and 37909.0. The first two of these give combination lines with some of the 5p terms and also with 4p ^{3}P$_2$. As the reality of these is not yet definitely confirmed they are omitted from the table. The two remaining levels are considered unreal as combinations with these occur elsewhere.

TABLE 2 (*a*)—Multiplets in Br II

$4p^4$	$(^4S)^3P_0$ 170279	$^3P_1$ 170980	$^3P_2$ 174119	$(^2D)^1D_2$ 162710	$5p(^4S)^5P_1$ 59436.2	$^5P_2$ 59300.9	$^5P_3$ 58942.8	$^3P_0$ 56284.7	$^3P_1$ 56557.5	$^3P_2$ 56351.4
$5s(^4S)^5S_2$ 80191.5		90788(1)	93918(9)		20755.3(10)	20890.6(10)	21248.7(10)		23634.0(3)	23840.0(6)
$^3S_1$ 75642.6	94628(5)	95329(20)	98470(20)		16206.3(1)	16341.7(3)		19358.0(8)	19085.1(10)	19290.9(10)
$5s(^3D)^3D_1$ 64690.8		106294(3)								
$^3D_2$ 64436.5			109683(5)	98284(0)						
$^3D_3$ 63740.8			110377(10)							
$^1D_2$ 61179.5		109802(4)	112933(2)	101530(10)						
$5s(^2P)^3P_0$ 52965.0		118015(1)								
$^3P_1$ 52561.0	117714(2)	118417(0)	121556(1)							
$^3P_2$ 51490.0		119488(3)	122627(5)							
$^1P_1$ 57333.0	112933(2)		116797(7)	105377(20)						
$4d(^4S)^3D_1$ 61723.1	108559(5)	109259(4)								
$^3D_2$ 62588.5		108394(6)	111528(10)							
$^3D_3$ 61658.5			112457(20)							
$6s(^4S)^5S_2$ 38324.7					21111.6(6)	20976.1(7)	20618.1(7)		18233.2(0)	18027.0(1)
$^3S_1$ 36511.0			137607(2)			22789.8(2)			20046.6(5)	19840.7(6)
$5d(^4S)^5D_0$ 33895.5					25540.8(6)					
$^5D_1$ 33896.3					25539.6(10)	25404.8(5)			22662.4(0)	22455.3(1)
$^5D_2$ 33612.0		137374(2)	140512(6)		25824.4(6)	25668.9(8)	25330.7(3)		22945.5(2)	22739.5(5)
$^5D_3$ 33824.5						25476.4(8)	25118.4(5)			
$^5D_4$ 33826.9							25116.1(10)			
$^3D_1$ 34668.8	135617(3)				24767.4(4)			21616.2(0)	21888.4(1)	
$^3D_2$ 33995.5		136987(2)	140125(1)		25441.0(6)	25305.4(7)	24947.2(3)		22562.1(4)	22356.0(5)
$^3D_3$ 34861.5			139266(0)			24439.3(2)	24081.3(3)			21490.2(6)
$6s(^2D)$										
$^3D_1$ 22660.7					36775.2(1)	36640.0(1)	36282.9(1)			33691.6(5)
$a=35992.0$		134992(4)						20290.5(4)	20565.7(3)	20359.8(2)

TABLE 2(*b*)—Multiplets in Br. II

5p(^{2}D)	$^3F_2$ 43509.1	$^3F_3$ 42810.3	$^3F_4$ 42373.3	$^3D_1$ 45442.7	$^3D_2$ 44153.1	$^3D_3$ 43465.1	$^3P_0$ 40544.4	$^3P_1$ 40517.9	$^3P_2$ 40840.9	$^1F_3$ 42430.3	$^1D_2$ 37511.3	$^1P_1$
5s(^{4}S) $^3S_1$ 75642.6	32133.9(0)						35098.4(0)	35124.8(2)	34801.5(4)			
5s(^{2}D) $^3D_1$ 64690.8	21181.6(7)			19248.0(6)	20537.6(4)		24146.6(6)	24173.1(6)				
$^3D_2$ 64436.5		21626.1(8)		18993.7(4)	20283.3(8)	20917.3(8)		23918.8(8)	23595.6(6)	22006.1(10)		21395.6(4
$^3D_3$ 63740.8		20930.4(5)	21367.5(10)		19587.9(2)	20275.6(9)			22899.9(20)	21310.4(1)		21141.2(0)
$^1D_2$ 61179.5	17670.4(1)	18369.3(3)		15736.4(8)	17026.4(2)			20661.7(2)	20338.7(0)	18749.3(10)	23668.2(20)	17884.3(7)
4d(^{4}S) $^3D_1$ 61723.1	18213.9(6)			16280.4(4)			21178.9(8)	21205.3(2)				18428.1(7)
$^3D_2$ 62588 5	19079.4(0)	19778.3(6)		17145.6(6)	18435.6(8)	19123.6(3)		22070.8(6)	21747.7(4)	20158.2(2)	25077.3(5)	
$^3D_3$ 61658,5	18149.1(1)	18848.1(7)	19285.2(4)		17505.3(5)	18193.1(6)			20817.4(6)		24146.6(6)	
5d(^{2}D) $^3G_3$ 18002.9	25506.2(7)	24808.0(2)										
$^3G_4$ 17966 7		24843.6(6)	24406.4(2)									
$^3G_5$ 17843.4			24529.9(5)									
$^3F_2$ 18527.4	24981.4(2)			26915.3(7)	25625.6(6)	24938.3(5)				23902.7(1)		24767.4(4)
$^3F_3$ 18082.7			24290.2(4)		26070.3(7)	25382.4(4)				24347.7(1)		
$^3F_4$ 17434.6		25375.5(7)	24938.3(5)			26030.5(4)				24995.3(3)		
$^3D_1$ 22761.2	20747.9(3)			22681 6(4)	21391.8(2)		17783.1(2)					
$^3D_2$ 22616.7	20892.3(0)	20193.5(3)		22826.0(3)	21536.3(6)	20848,2(4)		17900.8(2)				20533.9(0)
$^3D_3$ 21738.4	21770.7(0)	21071.9(3)	20634.7(5)		22414.6(2)	21726.6(6)			19102.4(5)			
$^3P_0$ 14861.1												
$^3P_1$ 16485.3	27023.8(1)			30581.6(0)	27668.0(3)			25656.8(3)				21626.1(8)
$^3P_2$ 15884.7				28956.7(1)	28269.1(3)	27580.4(2)		24031.7(5)	24354.9(2)			
									24956.6(3)			
$^3S_1$ 16393.1												
$^1G_4$ 19134.4		23676.6(2)		24156.1(2)	22866.4(3)			24124.1(0)	24447.8(2)	23295.9(7)		
$^1F_3$ 13231.3									27609.4(2)	29198.8(7)	24280.0(5)	
$^1D_2$ 21286.7		21523.6(2)								21143.6(5)	16224.7(6)	22008.5(5)
$^1P_1$ 20030.3											17481.0(5)	23264.9(5)
6s(^{2}D) $^3D_1$ 22660.7	20848.2(4)			22782.8(2)	21493.0(3)		17884.3(7)					20634.7(5)
$^3D_3$ 18094.0			24280.0(5)			25371.1(2)			22746.9(5)			
$^1D_2$ 19117.5						24347.7(1)				23312.3(2)	18393.8(6)	

In Tables 2 the wave numbers are from the measurements of Bloch and Lacroute for all lines except those in the vacuum region. The latter and the intensities for all the lines are from our plates. A few lines occur at more than one place in the scheme. The term values are also shown in the same tables, all the new terms identified in the present work being calculated relative to those established by Bloch and Lacroute.

A brief consideration of the term intervals may be of importance, as it gives an idea of the degree of approach of the Br II spectrum to the (*jj*) type of coupling. The deepest term 4pp ^3F is completely inverted and the interval ratio between its components, 4.4:1, is far from the theoretical value derived from the simple (1*s*) coupling. The variation of these intervals and of their ratio in SI and SeI like sectra shown in Tabie 2, supports the correctness of the identification.

TABLE 3

($^3P_2$—$^3P_0$) intervals

		Ratio			Ratio		
SI	572	1.74	ClII	994	1.58	A III	1574
Se I	2534	1.51	BrII	3838	1.39	Kr III	5313

The values of Br II are also in agreement with the limits as determined approximately by Kiess and de Bruin (1930) from the series of terms in Br I.

The terms in Br II as shown in Table I converge to the limits ^4S, ^2D and ^2P of Br III. The values of these limiting terms obtained by the authors (Ramanadham and Rao, 1944) are $^4S_{1\frac{1}{2}} - {}^2D_{1\frac{1}{2}} = 15042$ and $^2D_{2\frac{1}{2}} - {}^2P_{\frac{1}{2}} = 10613$ units. It is seen that the average differences between the following sets of terms,

5**s** (^4S) ^5S, $^3S \hookrightarrow$ 5**s** (^2D) ^3D ^1D.
5**d** (^4S) ^5D $^3D \hookrightarrow$ 5**d** (^2D) $^{1.3}G$ to $^{1.3}S$
5**p** (^4S) ^5P $^3P \hookrightarrow$ 5**q** (^2D) $^{1\text{-}3}F$ to $^{1,3}P$

are approximately 14400, 16000, and 15570 respectively. These are of the same order of magnitude as the difference $^4S - {}^2D$ of Bromine III. An accurate determination of the limits is not possible unless a long Rydberg series of terms is identified. The sources used in the present experimental work are not favourable for the production of such higher members. For this purpose an attempt is being made to study the hollow cathode spectrum of bromine and to extend the identification further to detect the terms based on the ^2P state of the ion. These will be dealt with in a later communication.

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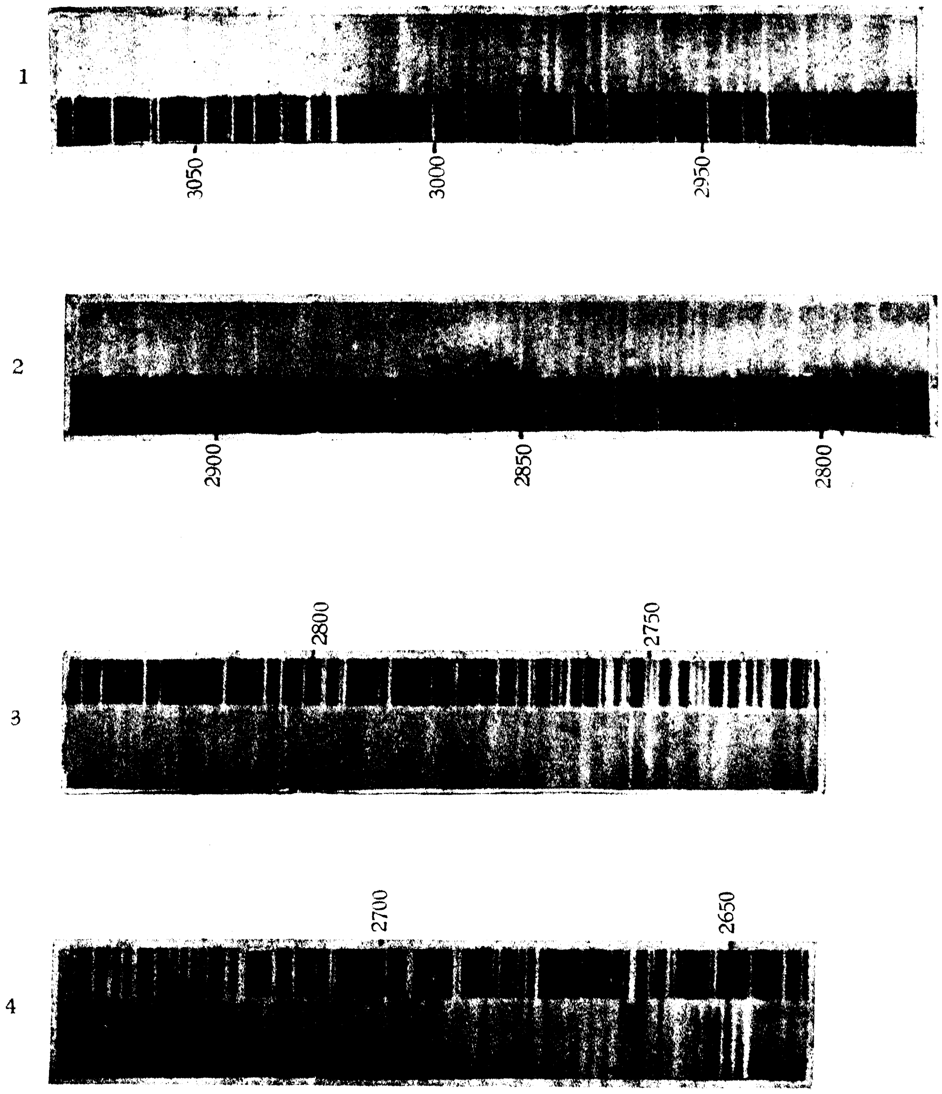

HgI Bands and Fe arc comparison
1 and 2 System C, 3 and 4 System D.