

# EMISSION SPECTRUM OF BROMINE EXCITED IN THE PRESENCE OF ARGON

## Part II. The Band System in the Region 3150–2970 Å

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### ABSTRACT

The wavelengths and wavenumbers of the band heads of the system 3150–2970 Å as obtained from the plates taken on the first order 21' grating spectrograph are given along with the vibrational analysis. This system is shown to be due to a transition from an upper electronic state at  $T_e = 48516 \text{ cm.}^{-1}$  with  $\omega'_e = 162.0 \text{ cm.}^{-1}$  and  $\omega'_e x'_e = 0.29 \text{ cm.}^{-1}$  to the well-known  ${}^3\Pi_u$  ( $O_u^+$ ) state at  $T_e = 15918 \text{ cm.}^{-1}$ . This lower state is common with that of the system 2950–2670 Å.

### INTRODUCTION

BROMINE when excited in the presence of argon was reported in an earlier paper<sup>1</sup> by the present authors to give: (1) a short discrete band system in the region 3150–2970 Å, (2) an extensive discrete band system in the region 2950–2670 Å, (3) a short and weak discrete band system in the region 2660–2590 Å and (4) a set of diffuse bands in the region 3340–3190 Å. The band system in the region 2950–2670 Å was analysed and discussed in that paper. The present paper deals with the analysis and discussion of the band system 3150–2970 Å.

### EXPERIMENTAL RESULTS

Using the same experimental set-up and conditions as described in the earlier paper, the band system 3150–2970 Å was photographed with a 21' grating spectrograph in the first order and also with a Hilger E<sub>1</sub> Littrow quartz spectrograph. This system is weaker than the 2950–2670 Å system discussed in the earlier paper and a part of it is usually overlapped by the traces of OH lines in the region 3064–3150 Å. It was, however, possible to get one plate without any trace of OH lines, but this plate showed only the intense part of the system.

The wavelengths and wavenumbers of the bands as measured from the plates taken on the 21' grating spectrograph are given in Table I along with

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their visually estimated relative intensities. The degradation of the bands in the system is not as clear as that in the 2950–2670 Å system. This may be because the vibrational frequencies of the upper and lower states for this system are much nearer to one another than those for the 2950–2670 Å system. Some of the bands appear to be degraded to long wavelength side and some towards short wavelength side while most of the bands do not appear to show any degradation. The error involved in the measurements of the band heads may be  $\pm 4$  or  $\pm 5 \text{ cm.}^{-1}$

TABLE I

*Wavelengths, wavenumbers and relative intensities of the bands in the system  $\lambda$  3150–2970 Å*

I	$\lambda_{\text{air}}$	$\nu_{\text{vac.}}$	I	$\lambda_{\text{air}}$	$\nu_{\text{vac.}}$
4	3140.4	31834	4	3087.4	32380
4	3138.5	31853	4	3083.5	32421
1	3136.3	31875	4	3082.7	32430
4	3134.1	31898	1	3076.2	32498
5	3132.5	31914	1	3069.5	32569
5	3131.1	31928	1	3067.1	32595
6	3126.7	31973	2	3060.1	32669
6	3125.1	31990	1	3058.8	32683
8	3122.5	32016	4	3057.7	32695
4	3121.8	32024	4	3057.2	32700
4	3120.4	32038	4	3056.6	32706
8	3119.9	32052	4	3054.3	32731
8	3118.4	32058	2	3053.9	32736
1	3117.2	32071	4	3052.4	32752
5	3113.8	32106	4	3052.1	32755
6	3112.1	32123	4	3050.7	32768
10	3110.7	32138	4	3050.3	32775
4	3109.1	32154	0	3049.2	32786
8	3106.9	32177	0	3048.1	32798
8	3105.1	32196	4	3047.0	32810
6	3101.2	32237	4	3046.3	32817
6	3099.3	32256	5	3045.0	32831
6	3098.6	32263	5	3044.4	32837
6	3097.5	32275	0	3043.0	32853
6	3096.8	32282	0	3041.4	32870
4	3095.9	32291	3	3039.8	32887
5	3095.2	32299	3	3037.8	32909
6	3093.4	32318	3	3037.0	32918
7	3091.5	32337	1	3036.4	32924
4	3090.2	32351			

TABLE I (Contd.)

I	$\lambda_{\text{air}}$	$\nu_{\text{vac.}}$	I	$\lambda_{\text{air}}$	$\nu_{\text{vac.}}$
1	3035.7	32932	0	3009.4	33220
1	3034.3	32947	2	3008.1	33234
1	3033.7	32953	1	3006.5	33252
0	3031.8	32974	1	3005.0	33268
2	3030.3	32990	1	3002.4	33297
2	3029.8	32996	1	3000.7	33316
1	3025.8	33040	2	2998.2	33344
1	3023.1	33069	2	2995.5	33374
?	3021.9	33082	2	2994.8	33382
1	3021.0	33092	2	2994.2	33388
2	3018.7	33117	1	2986.9	33470
1	3016.6	33140	2	2981.4	33532
2	3014.4	33164	1	2976.0	33592
2	3012.8	33182	0	2967.1	33693
1	3009.9	33214			

## THE VIBRATIONAL ANALYSIS

The vibrational analysis of the system is shown in Table II and the Frank-Condon parabola representing the intensity distribution in Table III. The analysis shows that all the bands in the system could be well represented as involving a transition from an upper initial state at  $T_e = 48516 \text{ cm.}^{-1}$  to the lower state at  $T_e = 15918 \text{ cm.}^{-1}$  with the same  $\Delta G''(v + \frac{1}{2})$  as given by Darbyshire<sup>2</sup> and Brown.<sup>3</sup> This state at  $15918 \text{ cm.}^{-1}$  is the well-known  ${}^3\Pi_u(\text{O}_u^+)$  state which forms the upper state of the visible absorption band system<sup>2</sup> in the region  $8672\text{--}5110 \text{ \AA}$  and is also the lower state of the band system  $2950\text{--}2670 \text{ \AA}$  discussed in the earlier paper.

The  $\Delta G''(v + \frac{1}{2})$  and  $\Delta G'(v + \frac{1}{2})$  values as obtained from the analysis are shown in Table II. The  $\Delta G(v + \frac{1}{2})$  values for the  ${}^3\Pi_u(\text{O}_u^+)$  level as obtained by Darbyshire and Brown from the visible absorption band system and those as obtained by the present authors from the analysis of the  $2950\text{--}2670 \text{ \AA}$  system are included in Table II for comparison. The existence of perturbation of  $v = 3$  and  $v = 4$  for the vibrational levels of the  ${}^3\Pi_u(\text{O}_u^+)$  state was indicated by Darbyshire<sup>2</sup> from the analysis of the visible absorption band system and is confirmed by the analysis of the present system as well as by that of the  $2950\text{--}2670 \text{ \AA}$  system. Because of this perturbation it will not be possible to find a single formula of the usual type representing accurately all the band heads in the system. However the vibrational constants of the two electronic states involved in the transition could be obtained fairly well

TABLE II  
The vibrational scheme for the band system  $\lambda$  3150–2970 Å

$v''$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	$\Delta G(v'')$	$\Delta G(v'')$ Cal.		
0	31595 165	32430 165	32275 155	32123 152	31973 150	31834 139															160.0	161.4	
1	32755 160	32595 165	32430 165	32282 148	32138 144	31990 148	31853 137															162.7	160.8
2	32918 164	32755 143	32595 163		32299 145	32154 138	32016 141	31875 163														162.5	160.2
3	33082 152	32918 149	32755 163	32595 160		32310 141	32177 139	32038 150	31898 160													156.4	159.7
4	33234 165	33069 165	32909 160	32755 159			32337 161	32196 141	32058 138	31914 144												158.7	159.1
5		33234 148	33069 145	32909 160	32768 141		32490 147	32351 149		32071 166												156.2	158.5
6		33382 150	33220 154	33069 151	32924 145	32775 149			32380 143	32237 131	32106 157	31973 133	31853 120									156.9	157.9
7		33532 161	33374 158	33220 159	33082 138	32932 150	32786 146				32263 125	32138 122	32016 161	31898 148								157.2	157.3
8		33693 161	33532 158	33374 158	33234 140	33092 142	32947 145	32790 149					32421 130	32291 124	32177 125	32052 124	31928					156.8	156.8
9			33532 144	33380 136	33252			32953 164	32817 136	32683 134												158.3	156.2
10						33252 135	33117 143	32974 137	32837 153	32700 152	32569 162							32029				154.7	155.6
11							33268		32990 137	32853 122	32711 150											153.0	155.0
12									33268 128	33140 157		32887 153	32755 132									157.0	154.4
13									33432 135	33297 133	33164 124	33040 131	32909 123	32786 117	32669 148							150.5	153.9
14									33592		33316 154	33182 134			32817 111	32706 147						154.3	153.3
15											33470 126	33344 130	33214			32853 161	32752						
16																				32695			
$\Delta G(v'')$	→ 163.4	161.0	154.6	143.1	144.1	141.4	142.0	139.3	136.8	134.5	129.1	124.8	122.0	120.5	117.0	107.0							
$\Delta G(v'')$ P.V.B.D.M.	→ 163.8	161.0	156.6	145.8	143.1	145.9	142.4	140.0	135.1	132.7	130.9	122.0	123.5	118.4	107.6	108.3							
$\Delta G(v'')$ O.S.B.D.M.	→ 164.6	160.5	156.5	145.0	144.2	144.1	143.2	138.8	135.8	129.8	128.7	122.6	122.1	119.8	107.9	108.5							

from the observed  $\Delta G(v + \frac{1}{2})$  values following the usual procedure. The vibrational constants  $\omega_0'' = 166.1 \text{ cm.}^{-1}$  and  $\omega_0'' x_0'' = 1.84 \text{ cm.}^{-1}$  obtained by Darbyshire from the analysis of the visible absorption band system are found to represent well the observed  $\Delta G''(v + \frac{1}{2})$  values of the present system as in the case of the 2950–2670 Å system. The observed  $\Delta G'(v + \frac{1}{2})$  values could be represented fairly well by the vibrational constants  $\omega_0' = 161.7 \text{ cm.}^{-1}$

TABLE III

The intensity distribution and Frank-Condon parabola of the bands in the system  $\lambda$  3150–2970 Å

$v'' \backslash v'$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
0	1	4	6	6	6	4													
1	4	1	4	6	10	6	4												
2	3	4	1		5	4	8	1											
3	?	3	4	1		6	8	4	4										
4	2	1	3	4			7	8	8	5									
5		2	1	3	4		1	4		1									
6		2	0	1	1	4			4	6	5	6	4						
7		2	2	0	?	1	0				6	10	8	4					
8		0	2	2	2	1	1	0			4	4	8	8	5				
9				2	2	1		1	4	1									
10							1	2	0	5	4	1							4
11								1		2	0	4							
12									1	1		3	4						
13									?	1	2	1	3	0	2				
14									1		1	2			5	4			
15											1	2	1			0	4		
16																			4

and  $\omega_0'x_0' = 0.29 \text{ cm.}^{-1}$ . The calculated  $\Delta G' (v + \frac{1}{2})$  values are included in Table II for comparison.

#### ISOTOPIC SHIFTS

As the vibrational frequencies for the upper and the lower states are not much different from one another, the isotopic shifts calculated for most of the bands observed do not come out to be more than 2 or 3  $\text{cm.}^{-1}$  which is within the experimental error of the measurements. This may be the main reason why no isotopic shifts could not be detected, though one expects two

weak isotopic components for each main band. Another probable reason why the isotopic shifts were not observable is that the band system is weak and a part of the system is overlapped by the OH lines.

## ELECTRONIC TRANSITION INVOLVED

The lower state of this 3150–2970 Å system like that of the 2950–2670 Å system described in the earlier paper is  $\sigma_g^2\pi_u^4\pi_g^3\sigma_u^3\pi_u$  ( $O_u^+$ ).

It is difficult to say definitely which electronic state is involved for the upper state unless the rotational structure of the bands of the system is studied, but the spectrum obtained in the present experiments does not show any rotational structure. However, as pointed out in the earlier paper with the help of the term scheme developed by Mulliken<sup>4</sup> for the iodine molecule and later on extended by Asundi and Venkateswarlu<sup>5</sup> for bromine molecule, the only configuration which is expected to give *gerade* states at about 50,000  $\text{cm}^{-1}$  is  $\sigma_g^2\pi_u^2\pi_g^4\sigma_u^2$ . This configuration gives the states  $^1\Sigma_g^+$  ( $O_g^+$ )  $^3\Sigma_g^-$  ( $O_g^+$ ,  $1_g$ ) and  $^1\Delta_{2g}$  of which the last one cannot combine with the  $^3\Pi_u$  ( $O_u^+$ ) state as the coupling is expected to be near that of Hund's case (c).  $^1\Sigma_g^+$  ( $O_g^+$ ) is expected to lie higher than  $^3\Sigma_g^-$  ( $O_g^+$ ,  $1_g$ ) and it had been tentatively attributed to the state at  $T_e = 51802 \text{ cm}^{-1}$  which forms the upper level of the band system 2950–2670 Å.  $^3\Sigma_g^-$  ( $O_g^+$  or  $1_g$ ) may be tentatively assigned to the state at  $T_e = 48516 \text{ cm}^{-1}$  which forms the upper state of the present system 3150–2970 Å. This state may also be expected to be ionic like the  $^1\Sigma_g^+$  ( $O_g^+$ ) state at  $51802 \text{ cm}^{-1}$ .

## REFERENCES

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