

# THE EMISSION SPECTRUM OF IODINE BROMIDE EXCITED IN THE PRESENCE OF ARGON

Part I. The Band System in the Regions 5425–5360 Å, 4520–4415 Å  
and 4120–4010 Å

BY PUTCHA VENKATESWARLU, F.A.Sc., AND R. D. VERMA\*

(Department of Physics, Muslim University, Aligarh)

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## ABSTRACT

I<sub>2</sub>Br vapour was excited in the presence of argon by an uncondensed transformer discharge. Four band systems were obtained in the regions 5425–5360 Å, 4520–4415 Å, 4120–4010 Å and 3915–3540 Å of which the first three are discussed in this paper. The wavelengths and wavenumbers of the band heads in three systems as measured from the plates obtained with a 3-prism Steinheil glass spectrograph are given along with their visually estimated relative intensities. The three band systems, which are new, are analysed and the following vibrational constants expressed in cm.<sup>-1</sup> are obtained:

Band system	$\nu_0$	$\omega_0''$	$\omega_0''x_0''$	$\omega_0''y_0''$	$\omega_0'$	$\omega_0'x_0'$
5425–5360 Å	18613	65.5	0.24	–0.01	43.0	0.026
4520–4415 Å	22312	65.5	0.24	–0.01	77.0	0.5
4120–4010 Å	24540	160.6	1.125	..	128.4	0.1

The lower state of the first two systems has been identified with the (O<sup>+</sup>) state at 16814 cm.<sup>-1</sup> reported earlier by Brown from a study of the absorption bands in the visible region.

## INTRODUCTION

ASUNDI and Venkateswarlu<sup>1</sup> excited I<sub>2</sub>Br vapour by an uncondensed transformer discharge and recorded a number of continuous bands in the region 5200–2300 Å some of which correspond to some fluorescence bands obtained

\* Formerly a Research Assistant of the Uttar Pradesh Government and now a Senior Research Fellow of the Council of Scientific and Industrial Research, Government of India.

earlier by Filippov.<sup>2</sup> Haranath and Rao,<sup>3</sup> by exciting IBr vapour with a condensed transformer discharge reported recently about 40 bands in the region 3900–3800 Å and explained them as due to a transition from an upper state at 38306 cm.<sup>-1</sup> to the lower state at 12230 cm.<sup>-1</sup>, established earlier by Brown<sup>4</sup> from a study of absorption in the near infrared region. They also obtained some bands in the region 1975–1740 Å, which were reported to correspond to those obtained by Cordes and Spomer<sup>5</sup> in absorption.

Iodine, bromine and chlorine are known<sup>6</sup> to give groups of diffuse bands or continua when excited without the presence of a foreign gas. But when they are excited in the presence of a foreign gas, they give new discrete band systems. Filippov<sup>2</sup> could not detect any such discrete band system by exciting IBr vapour in the presence of N<sub>2</sub>. This is probably because the pressure of N<sub>2</sub> used by him might not have been high enough and also because the dispersion of the spectrograph used was very small. As the results that had been obtained in this laboratory by exciting I<sub>2</sub>, Br<sub>2</sub> and Cl<sub>2</sub>\* in the presence of argon were encouraging, the problem of studying the spectrum of IBr excited under similar conditions has been taken up and the results obtained in the region 6000–4000 Å are discussed in this paper.

#### EXPERIMENTAL RESULTS

Iodine bromide was excited in the presence of argon with an uncondensed transformer discharge and the spectrum obtained was photographed with a 3-prism Steinheil glass spectrograph with long camera and a Hilger E<sub>1</sub> Littrow quartz spectrograph. The other experimental details are similar to those described earlier in the case of bromine.<sup>7</sup> As the pressure of argon is increased the continuous bands that one gets by exciting the IBr vapour without the presence of argon, slowly disappear and a new spectrum results. The new spectrum consists of short band systems in the regions (1) 5425–5360 Å, (2) 4520–4415 Å and (3) 4120–4010 Å together with an extensive band system in the region 3915–3540 Å. Besides these systems, the 2950–2670 Å band system of Br<sub>2</sub> and the 4400–4000 Å and 3450–3015 Å band systems of I<sub>2</sub> discussed in the earlier papers<sup>7, 8</sup> are also detected. The band systems of I<sub>2</sub> appear, however, more strongly than that of Br<sub>2</sub>. It was found that by the introduction of fresh samples of IBr vapour at frequent intervals the intensity of the I<sub>2</sub> band systems could be considerably decreased and of IBr systems enhanced.

Figure 1 shows the spectrum obtained by exciting IBr vapour in the presence of argon as photographed with a Hilger E<sub>1</sub> Littrow quartz spectro-

\* Recent work that is in progress in this laboratory shows that Cl<sub>2</sub> excited in the presence of argon shows a discrete band system in the region 2600–2400 Å.

graph in the region 4800–3350 Å. The spectrum of I<sub>2</sub> obtained under similar conditions in the same region is also shown for comparison. Bromine excited in the presence of argon does not show any band system in this region. The band system 5425–5360 Å, 4520–4415 Å and 3915–3540 Å can easily be attributed to IBr because I<sub>2</sub> and Br<sub>2</sub> excited under similar conditions do not show any discrete band systems in these regions. The 4120–4010 Å band system is sometimes overlapped by the weak bands of the 4400–4000 Å system of I<sub>2</sub> whose strong part lies in the region 4300–4200 Å. But by introducing fresh samples of IBr vapour at frequent intervals and by adjusting the time of exposure it is possible to photograph the spectrum in such a way that the I<sub>2</sub> bands are visible in the region 4300–4200 Å, and not in the region 4120–4010 Å so that the 4120–4010 Å system of IBr is obtained without any trace of I<sub>2</sub> bands.

#### THE BAND SYSTEMS IN THE REGIONS 5425–5360 Å AND 4520–4415 Å

*The 5425–5360 Å system.*—Figure 2 shows the enlargement of the spectrum in the region 5425–5360 Å obtained with a 3-prism Steinheil glass spectrograph. The bands are degraded to longer wavelengths. The wavelengths and wavenumbers of the band heads are listed in Table I along with

TABLE I  
*Wavelengths, wavenumbers and relative intensities of the bands in the system 5425–5360 Å*

I	$\lambda_{\text{air}}$	$\nu_{\text{vac}}$	I	$\lambda_{\text{air}}$	$\nu_{\text{vac}}$
1	5422.1	18438	3	5393.0	18537
1	5420.0	18451	3	5387.6	18556
2	5413.1	18469	6	5381.4	18577
2	5409.9	18480	2	5378.7	18587
2	5405.1	18496	8	5373.8	18604
2	5399.2	18516	2	5369.8	18618
2	5397.5	18522	8	5362.6	18643

their visually estimated relative intensities. The measurements were made from the plates taken with the 3-prism Steinheil glass spectrograph. The error in the measurements of band heads may be  $\pm 2 \text{ cm.}^{-1}$ . The vibrational

analysis of the bands is shown in Table II. The bands fall in sequences, the strongest of which is represented as the  $\Delta v = 0$  sequence.

TABLE II

The vibrational scheme for the bands in the system 5425-5360 Å

$v'' \backslash v'$	0	1	2	3	4	$\Delta G'(v + \frac{1}{2})$ Obs.	$\Delta G'(v + \frac{1}{2})$ Cal.
0	18604 39	67 18537 40	68 18469 47			42.0	43.0
1	18643	66 18577 41	61 18516 40	65 18451 45		42.0	42.9
2		18618	62 18556 48	60 18496 41	58 18438 42	43.7	42.9
3			18604 39	67 18537 50	57 18480 42	43.7	42.8
4			18643 56	18587 65	18522		
$\Delta G''(v + \frac{1}{2})$ Obs.	66.5	63.6	62.0	60.0			
$\Delta G''(v + \frac{1}{2})$ Cal.	65.0	64.5	63.9	63.2			

The 4520-4415 Å system.—The enlargement of the spectrum in the region 4520-4415 Å obtained with a 3-prism Steinheil glass spectrograph is shown in Fig. 3. The degradation of the bands in general is not clear, though some of the bands appear to be degraded to longer wavelengths and a few to the shorter wavelengths. The wavelengths and wavenumbers of band heads as obtained from the plates taken on the 3-prism Steinheil glass spectrograph are tabulated in Table III along with their visually estimated relative intensities. The vibrational analysis of the bands is given in Table IV. The error in measurements of band heads may be  $\pm 3 \text{ cm.}^{-1}$ . The bands of this system like those of the 5425-5360 Å system fall mainly in sequences and the sequence starting with the strongest bands is represented as the  $\Delta v = 0$  sequence.

The  $\Delta G''(v + \frac{1}{2})$  values obtained for the 5425-5360 Å system are quite close to those obtained for the 4520-4415 Å system which suggests that the

TABLE III  
*Wavelengths, wavenumbers and relative intensities of the  
 bands in the system 4520–4415 Å*

I	$\lambda_{\text{air}}$	$\nu_{\text{vac}}$	I	$\lambda_{\text{air}}$	$\nu_{\text{vac}}$
2	4518.9	22123	3	4458.8	22421
2	4510.3	22165	3	4455.6	22437
2	4505.8	22187	3	4450.0	22466
2	4502.7	22203	3	4447.6	22478
2	4493.4	22249	3	4446.4	22484
5	4490.1	22265	6	4445.1	22490
6	4488.0	22275	6	4443.3	22500
8	4484.5	22293	2	4440.7	22513
8	4482.2	22304	2	4438.4	22524
10	4479.0	22320	4	4437.2	22530
10	4478.2	22324	5	4435.8	22538
5	4475.1	22340	2	4432.6	22554
5	4471.1	22360	1	4431.2	22561
1	4468.4	22373	0	4430.5	22565
1	4466.0	22385	1	4424.8	22594
1	4464.4	22393	0	4422.6	22605
1	4463.4	22398	0	4415.1	22643

two systems have a common lower state. It is quite likely that the lower state of these two systems is the ( $O^+$ ) state at  $16880 \text{ cm.}^{-1}$  reported by Brown<sup>4</sup> from the study of the visible absorption bands. The  $\Delta G(v + \frac{1}{2})$  values obtained by Brown for this state from  $v = 8$  to  $v = 37$  are plotted against  $v$  along with the  $\Delta G''(v + \frac{1}{2})$  values of the 4520–4415 Å system from  $v = 0$  to  $v = 7$ . The  $\Delta G''(v + \frac{1}{2})$  values of the system 5425–5360 Å from  $v = 0$  to  $v = 3$  are also plotted in the same graph (see Fig. 4). It was found that within the experimental error all the points plotted can be fairly represented by a smooth curve and all the  $\Delta G(v + \frac{1}{2})$  values can be expressed by the vibrational constants  $\omega_0 = 65.3 \text{ cm.}^{-1}$ ,  $\omega_0 x_0 = 0.23 \text{ cm.}^{-1}$  and  $\omega_0 y_0 = 0.01 \text{ cm.}^{-1}$ . The calculated and observed  $\Delta G''(v + \frac{1}{2})$  are given in Tables II and IV for comparison. All the bands of the 5425–5360 Å system can be

TABLE IV

The vibrational scheme for the bands in the system 4520-4415 Å

$v' \backslash v''$	0	1	2	3	4	5	6	7	8	$\Delta G'$ ( $v+\frac{1}{2}$ ) Obs.	$\Delta G'$ ( $v+\frac{1}{2}$ ) Cal.
0	22320	22249	22187	22123							
	71	62	64								
	73	75	78	80						76.5	76.0
1	22393	22324	22265	22203							
	69	59	62								
	73		75	72						73.5	75.0
2	22466	..	22340	22275							
			65								
	72									72.0	74.0
3	22538	22478	..	..	22293	..	22165				
	60										
		76								71.5	73.0
4		22554	22484	22421	22360	22304	..				
		70	63	61	56						
			77	69	77	69				73.0	72.0
5			22561	22490	22437	22373	22304	22249			
			71	53	64	69	55				
				75	63	64	81	71		70.8	71.0
6				22565	22500	22437	22385	22320	22265		
				65	63	52	65	55			
						76		73		74.5	70.0
7					..	22513	..	22393	..		
										..	69.0
8					22643	..	22524	..	22398		
										..	68.0
9								22530	..		
								64		64.0	67.0
10								22594	22538		
									56		
									67	67.0	66.0
11									22605		
$\Delta G''$ ( $v+\frac{1}{2}$ ) Obs.	66.7	63.7	65.0	59.7	61.0	60.5	60.0	55.5			
$\Delta G''$ ( $v+\frac{1}{2}$ ) Cal.	65.0	64.5	63.9	63.2	62.5	61.7	60.9	60.1			

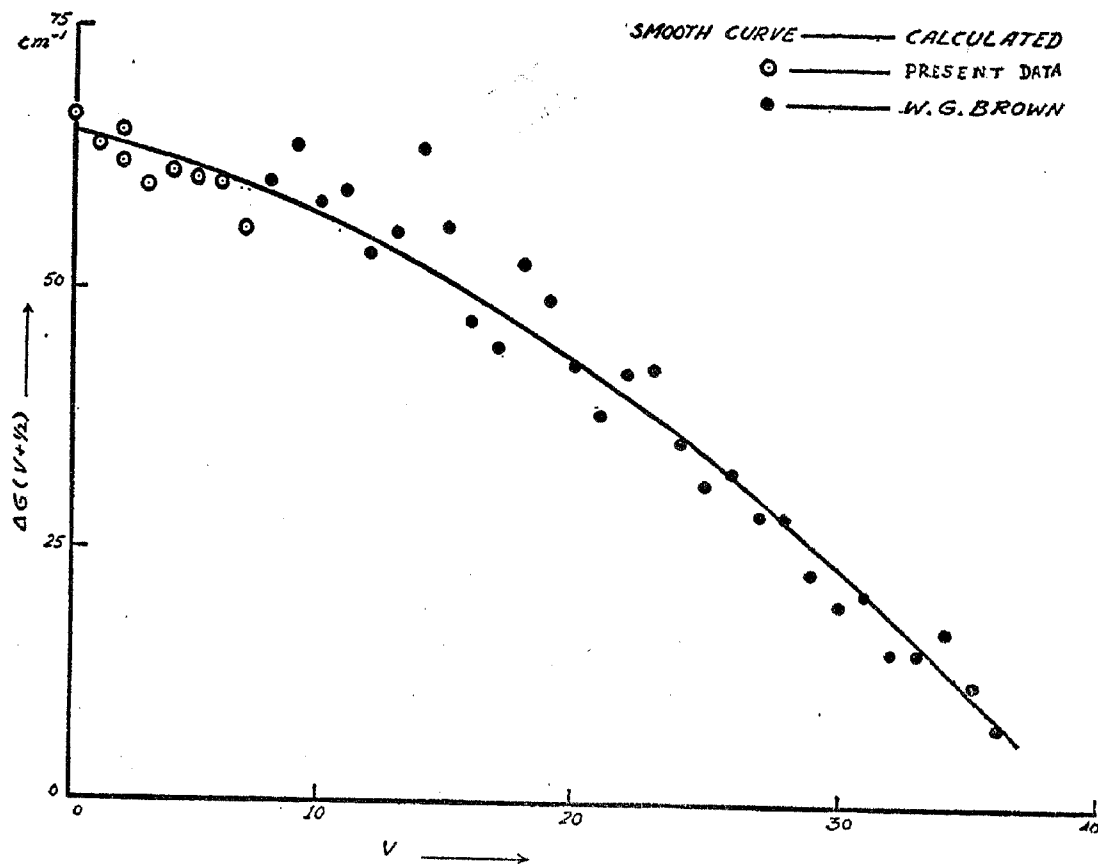


FIG. 4. The graph showing the  $\Delta G(v + \frac{1}{2})$  versus  $v$  of  $(O^+)$  state at  $T_e = 16814 \text{ cm.}^{-1}$  fairly well represented by the formula  $v = 18602 + (43.0 v' - 0.026 v'^2) - (65.3 v'' - 0.23 v''^2 - 0.01 v''^3)$  and similarly those of the 4520–4415 Å system can be represented by the equation

$$v = 22318 + (76.5 v' - 0.5 v'^2) - (65.3 v'' - 0.23 v''^2 - 0.01 v''^3)$$

As the lowest level of the  $(O^+)$  state observed by Brown is  $v = 8$ , he obtained  $T_e = 16880 \text{ cm.}^{-1}$  of the state by extrapolation from  $v = 8$  to  $v = 0$  assuming that the  $\Delta G(v + \frac{1}{2})$  remains constant as  $60 \text{ cm.}^{-1}$  for those levels. It is not necessary now to use such an extrapolation, since the  $\Delta G''(v + \frac{1}{2})$  values from  $v = 0$  to  $v = 7$  are observed in the present experiments. Using the vibrational constants obtained from the present work and taking into consideration the experimental data of Brown regarding the position of the level  $v = 8$ , the  $\omega_e$  and  $T_e$  for the state  $(O^+)$  are obtained to be  $65.5 \text{ cm.}^{-1}$  and  $16814 \text{ cm.}^{-1}$  respectively.\*

\* According to Brown's observation the position of the level  $v = 8$  of the  $(O^+)$  state above the  $v = 1$  of the ground state, is at  $16947.8 \text{ cm.}^{-1}$ . Using  $\omega_0 = 267.6 \text{ cm.}^{-1}$  for the ground state, the position of the level  $v = 8$  of the  $(O^+)$  state above the level  $v = 0$  of the ground state, is at  $17214.6 \text{ cm.}^{-1}$ . The height of the level  $v = 8$  over the level  $v = 0$  of the  $(O^+)$  state as obtained from the vibrational constants,  $\omega_0 = 65.3 \text{ cm.}^{-1}$ ,  $\omega_0 l_0 = 0.23 \text{ cm.}^{-1}$  and  $\omega_0 y_0 = 0.01 \text{ cm.}^{-1}$  is  $502.6 \text{ cm.}^{-1}$ . This gives  $T_e = 16712 \text{ cm.}^{-1}$  from which  $T_e$  can be calculated as  $16814 \text{ cm.}^{-1}$ .

Thus the position of the upper level of the 5425–5360 Å system is at  $T_e = 35427 \text{ cm.}^{-1}$  and that of the 4520–4415 Å system is  $T_e = 39126 \text{ cm.}^{-1}$

THE BAND SYSTEM IN THE REGION 4120–4010 Å

Figure 5 shows the enlargement of the spectrum in the region 4120–4010 Å taken with 3-prism Steinheil glass spectrograph. The spectrum consists of bands degraded to longer wavelengths and also bands degraded to shorter wavelengths. The wavelengths and wavenumbers of band heads obtained from the plates taken with a 3-prism Steinheil glass spectrograph are given in Table V along with their visually estimated relative intensities.

TABLE V  
*Wavelengths, wavenumbers and relative intensities of the bands in the system 4120–4010 Å*

I	$\lambda_{\text{air}}$	$\nu_{\text{vac}}$	I	$\lambda_{\text{air}}$	$\nu_{\text{vac}}$
1	4117.8	24278	6	4062.4	24609
2	4104.9	24355	4	4060.5	24621
3	4099.3	24387	3	4059.4	24627
3	4096.9	24402	4	4058.4	24633
8	4091.1	24437	2	4055.5	24651
8	4086.5	24464	5	4055.0	24654
4	4084.0	24479	2	4050.7	24680
5	4082.8	24486	3	4048.7	24692
8	4081.4	24495	0	4047.6	24699
10	4076.2	24526	1	4045.8	24710
10	4073.5	24542	1	4043.3	24725
8	4071.0	24557	2	4043.0	24727
10	4069.8	24564	1	4041.2	24738
3	4069.3	24567	0	4040.2	24744
2	4068.0	24575	1	4035.3	24774
4	4066.2	24586	1	4034.5	24779
7	4065.2	24592	1	4027.5	24822
4	4063.4	24603	1	4015.2	24898
			1	4014.1	24905



The error in measurements of band heads may be  $\pm 1.5 \text{ cm.}^{-1}$ . The Deslandres scheme of the bands degraded to longer wavelengths is shown in Table VI. The bands fall in sequences, the strongest of which is represented as the  $\Delta v = 0$  sequence and the strongest band as the (0, 0) band. All the bands can fairly well be represented by the formula  $\nu = 24524 + (128.3 v' - 0.1 v'^2) - (159.45 v'' - 1.125 v''^2)$  with  $v' = 0 - 5$  and  $v'' = 0 - 4$ .

TABLE VI

*The vibrational scheme for the bands degraded to longer wavelengths in the system 4120-4010 Å*

$v'' \backslash v'$	0	1	2	3	4	$\Delta G' (v+\frac{1}{2})$ Obs.	$\Delta G' (v+\frac{1}{2})$ Cal.
0	24526 128					128.0	128.0
1	24654 125	159 24495 126				125.5	127.8
2	24779 126	158 24621	157 24464 128			127.0	127.6
3	24905	..	24592 155	24437 127		127.0	127.4
4				24564		..	127.2
5					24542		
$\Delta G'' (v+\frac{1}{2})$ Obs.	158.5	157.0	155.0	..			
$\Delta G'' (v+\frac{1}{2})$ Cal.	158.2	155.8	153.4	151.0			

The Deslandres scheme for the bands degraded to shorter wavelengths is shown in Table VII where  $n'$  and  $n''$  are arbitrary. These bands also fall in sequences. It was found that these bands can also be represented by the same formula as that for the bands in Table VI with  $n' = 19$  and  $n'' = 17$ . Therefore it seems likely that the bands of Table VII may be the tail bands of those shown in Table VI.

TABLE VII  
The vibrational scheme for the bands degraded to shorter wavelengths in the system 4120-4010 Å

$v'$	$v''$	$n''+0$	$n''+1$	$n''+2$	$n''+3$	$n''+4$	$n''+5$	$n''+6$	$n''+7$	$n''+8$	$n''+9$	$n''+10$	$n''+11$	$n''+12$	$n''+13$	$n''+14$	$\Delta G''$ Cal. ( $v+\frac{1}{2}$ )	$\Delta G''$ ( $v+\frac{1}{2}$ ) Obs.
$n'+0$	..	24567 125	..	..	..	..	..	..	..	..	..	..	..	..	..	..	125.0	124.4
$n'+1$	..	24692	24575	..	24355	..	..	..	..	..	..	..	..	..	..	..	124.0	124.2
$n'+2$	..	117	124	24699	24586	24479	..	..	..	..	..	..	..	..	..	..	123.7	124.0
$n'+3$	..	112	107	113	107	117	24822	24710	24608	24486	..	24278	..	..	..	..	122.0	123.8
$n'+4$	..	116	107	123	124	124	24725	24609	..	24402	124	..	..	..	..	..	129.0	123.6
$n'+5$	..	111	129	24738	24627	..	..	..	..	..	..	..	..	..	..	..	..	123.4
$n'+6$	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	123.2
$n'+7$	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	125.0	123.0
$n'+8$	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	122.8
$n'+9$	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	123.0
$n'+10$	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	122.6
$n'+11$	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	124.0
$\Delta G''$ ( $v+\frac{1}{2}$ ) Obs.		117.0	112.5	107.0	116.5	111.0	..	..	..	..	..	..	..	..	..	..	..	..
$\Delta G''$ ( $v+\frac{1}{2}$ ) Cal.		116.9	114.4	112.0	109.5	107.1	104.6	102.2	99.7	97.3	94.8	92.4	90.0	87.6	85.1	..	..	..

Note:—The bands expected for the positions marked (\*) in the above table are overlapped by the strong bands degraded to longer wavelengths falling at the same positions.

It may be mentioned that it was not possible to identify any of the two states involved in the 4120-4010 Å system with any of the known levels of the IBr molecule.

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