

# EMISSION SPECTRUM OF BROMINE EXCITED IN THE PRESENCE OF ARGON—PART I

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## ABSTRACT

Bromine was excited by an uncondensed transformer discharge in the presence of argon. The spectrum obtained was found to be different from what one gets without the presence of a foreign gas and consists of (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 system in the region 2660–2590 Å and a set of diffuse bands in the region 3340–3190 Å. The wavelengths and wave numbers of the band heads of the system 2950–2670 Å, as obtained from the measurements of the plates taken on the first order 21-ft. 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 51802 cm.<sup>-1</sup> with  $\omega_e' = 150.5$  cm.<sup>-1</sup> and  $\omega_e'x_e' = 1.15$  cm.<sup>-1</sup> to the well known  $^3\Pi_u$  ( $O_u^+$ ) state at 15918 cm.<sup>-1</sup>

## INTRODUCTION

THE emission spectrum obtained by electrical excitation of bromine vapour is known to consist of bands degraded to longer wavelength in the region<sup>1,2</sup> 6700–4400 Å and a number of groups of diffuse bands and continua<sup>3–6</sup> in the region 4200–2000 Å. According to Uchida and Ota<sup>1</sup> and also according to Haranath and Rao<sup>2</sup> these bands could be analysed into two systems which arise from two different initial states and involve a common final level which is different from the ground level. The groups of diffuse bands and continua were explained by Venkateswarlu<sup>5</sup> as due to transitions from different stable upper states to various repulsive states dissociating into normal  $^2P + ^2P$  bromine atoms. The electrical and fluorescent excitations of iodine vapour are known to give a discrete band system in emission in the region<sup>6,7</sup> 6700–5000 Å and groups of diffuse bands<sup>8,9</sup> in the region 4800–2400 Å. The discrete band system in emission is known to be completely identical with that in absorption. The groups of diffuse bands were explained by Venkateswarlu<sup>9</sup> as due to transitions from different upper stable states to various lower repulsive states dissociating into  $^2P + ^2P$  normal iodine atoms. It was known by experiments of earlier workers<sup>10–12</sup> that the spectrum obtained by fluorescent excitation of a mixture of iodine and nitrogen is completely different from the fluorescent spectrum of pure iodine vapour.

Elliott<sup>12</sup> obtained four band systems in the regions 4630–4440 Å, 4321–4041 Å, 3450–3040 Å and 2730–2530 Å. Waser and Wieland<sup>13</sup> excited iodine vapour in the presence of argon gas by a high frequency discharge and reported the last three of the systems obtained by Elliott in fluorescence in the presence of nitrogen. Venkateswarlu<sup>14</sup> later excited iodine by transformer discharge and obtained the above three band systems and also a weak system in the region 2785–2750 Å.

Cameron and Elliott<sup>15</sup> excited bromine in the presence of active nitrogen and reported that the continuum at 2900 Å is superposed by a set of diffuse bands with a separation of about  $147 \text{ cm.}^{-1}$ . He, however, did not give the wavelengths or wave numbers of these bands. Because of the above mentioned results obtained by earlier workers in iodine it was expected that new band systems could be well developed if bromine was excited in the presence of argon. This investigation was therefore taken up in this laboratory and the results obtained are given in this paper.

#### EXPERIMENTAL DETAILS

Bromine vapour was excited in the presence of argon by an uncondensed transformer discharge. The discharge tube was made of pyrex glass and was 50 cm. in length and 0.8 cm. in diameter. It was fitted with a quartz window on one side and a silvered quartz mirror on the other side. Tungston electrodes were used and were found to be quite satisfactory. Band systems obtained were however checked up by using aluminium electrodes also. Argon marked spectrally pure was obtained from Oxygen Acetylene Co. Bromine was prepared by heating cupric bromide. The vapour was dried by allowing it to pass over  $\text{P}_2\text{O}_5$  tube attached to the system.

It was found that with the increase of the pressure of argon the original spectrum consisting of the discrete band system of bromine in the visible region and the groups of diffuse bands in the region 4200–2000 Å goes down in intensity and new spectrum appears. By adjusting the pressure of argon it was possible to eliminate the original spectrum (except for faint traces at the intense portions) and obtain only the new spectrum. It may be mentioned that the pressures of argon or bromine in the discharge tube were not measured in these experiments, but the relative pressures were adjusted by the visual observation of the colour and the shape of the discharge.

The new spectrum consists of (1) a short discrete band system in the region 3150–2970 Å which is overlapped by the traces of OH bands, (2) an extensive discrete band system 2950 Å–2670 Å, (3) a short and weak discrete band system in the region 2660–2590 Å and (4) a set of diffuse

bands\* with intensity maxima at 3211, 3235, 3263, 3292 and 3335 Å. In this paper the analysis of the band system in the region 2950–2670 Å only will be discussed. The discussion of the other systems will be taken up at a later stage when further work is completed.

It was found that the discrete band system 2950–2670 Å could be well developed in intensity and sharpness by adjusting the pressures of the constituent gases such that the discharge was unstationary twisted ribbon-like in shape and pinkish white in colour. It may be mentioned that the band system is usually overlapped by a continuum which extends to shorter wavelengths. This continuum could be well diminished in intensity if the discharge tube is effectively cooled. The origin of this continuum appears to be similar to that of the continua obtained and explained by Uchida<sup>16</sup> in halogens at high temperatures. This means that probably during the discharge a certain amount of molecular bromine is converted into bromine atoms in normal and excited states which on recombination by the two body collision process emit the continuum. However, if the tube is cooled effectively the kinetic energy of the excited and normal atoms is reduced which in turn diminishes the drift velocity and hence makes the two body collision recombination rare.

The spectra were taken in stagnant condition, but when long exposures were needed fresh quantities of bromine and argon were introduced after every four hours or so. The discharge tube was cooled by using a water jacket between the two electrodes, while the electrodes were cooled by an electric fan.

The spectra were first taken with a medium Hilger quartz spectrograph which has a dispersion of 12.5 Å per mm. at 2900 Å and then with a Hilger E<sub>1</sub> Littrow quartz spectrograph which has a corresponding dispersion of about 4.4 Å per mm. The band system was then photographed with an Eagle mounting 21-ft. grating spectrograph in the first and second orders with the dispersion of 2.6 Å per mm. and 1.3 Å per mm. respectively. Fig. 1 shows the spectra obtained in the first order. The plates were measured with a Carl Zeiss Abbe comparator.

The wavelengths and wave numbers of all the bands, as obtained from an average of four measurements of the plates taken on the first order 21-ft. grating spectrograph, are given in Table I along with their visually estimated relative intensities. Though the individual measurements did not differ

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\* Electrical excitation of bromine vapour without the presence of argon were reported<sup>5</sup> to show in this region certain diffuse bands with their intensity maxima at 3367, 3337, 3269 and 3239 Å. It is to be ascertained by further work whether any of these bands are common with those obtained in the presence of argon.

TABLE I  
*Wavelengths, wave numbers and relative intensities of the bands in the system 2950-2670 Å.*

I	$\lambda_{air}$	$\nu_{vac}$	I	$\lambda_{air}$	$\nu_{vac}$
1	2952.5	33860	6	2902.0	34449
2	2952.0	33866	4	2900.6	34466
1	2951.6	33870	0	2900.0	34471
0	2948.0	33911	4	2899.4	34480
1	2946.5	33929	4	2898.8	34487
1	2945.4	33941	0	2898.4	34492
2	2944.8	33948	3	2896.8	34511
0	2944.2	33955	4	2895.9	34521
0	2940.7	33996	2	2894.3	34541
1	2940.4	33999	7	2893.7	34548
0	2940.0	34004	0	2893.3	34553
2	2939.6	34008	2	2892.3	34565
3	2939.2	34013	3	2891.9	34569
0	2938.7	34019	2	2891.4	34575
0	2937.3	34035	0	2891.0	34580
0	2933.7	34077	5	2889.9	34593
6	2933.4	34080	4	2888.6	34609
1	2933.1	34084	2	2887.2	34626
5	2932.7	34088	6	2883.2	34674
1	2932.1	34095	7	2881.8	34690
4	2929.3	34128	7	2881.6	34693
5	2928.7	34135	2	2881.2	34698
1	2928.1	34142	0	2880.0	34712
2	2926.7	34158	1	2879.1	34723
9	2924.2	34187	1	2877.5	34742
7	2923.6	34194	0	2875.2	34770
2	2922.9	34203	5	2871.9	34810
5	2920.7	34228	4	2871.0	34821
8	2920.0	34237	3	2870.2	34830
5	2919.3	34245	0	2869.3	34842
0	2918.3	34257	0	2867.4	34865
4	2916.5	34278	4	2866.0	34882
0	2915.4	34291	2	2864.2	34904
10	2914.2	34304	2	2861.7	34934
10	2913.9	34308	4	2860.3	34951
1	2913.5	34313	5	2859.7	34958
0	2912.6	34324	3	2858.9	34968
1	2911.6	34335	0	2858.5	34973
1	2910.8	34345	0	2857.9	34980
0	2909.2	34364	3	2854.8	35018
5	2908.0	34378	0	2853.0	35041
5	2907.3	34386	1	2851.8	35055
3	2905.2	34411	1	2850.1	35076
6	2904.5	34419	2	2849.0	35090
6	2904.0	34425	5	2848.0	35102
4	2903.4	34432	4	2847.6	35107

TABLE I—(Contd.)

I	$\lambda_{air}$	$\nu_{vac}$	I	$\lambda_{air}$	$\nu_{vac}$
3	2846.4	35122	2	2769.3	36100
1	2843.6	35156	1	2768.7	36107
3	2836.5	35244	4	2767.9	36118
5	2835.8	35253	0	2767.2	36127
2	2835.5	35257	2	2766.4	36137
1	2834.7	35267	2	2765.7	36147
1	2824.7	35392	0	2764.2	36166
2	2824.1	35399	2	2762.6	36187
2	2813.5	35532	0	2761.7	36199
3	2813.0	35539	0	2760.1	36220
2	2812.5	35545	3	2759.2	36232
1	2808.3	35598	4	2758.3	36244
0	2803.8	35655	4	2757.1	36259
3	2802.6	35671	0	2756.3	36270
3	2802.0	35678	0	2755.7	36278
3	2801.5	35685	0	2753.4	36308
0	2800.9	35692	0	2751.7	36330
0	2800.0	35704	2	2750.1	36352
1	2799.4	35711	3	2749.6	36358
0	2794.7	35771	0	2746.9	36394
0	2794.0	35780	2	2745.9	36407
1	2793.4	35788	1	2742.5	36452
1	2793.0	35793	0	2740.9	36474
0	2792.4	35801	0	2737.8	36515
0	2791.9	35807	2	2736.1	36538
2	2791.3	35815	2	2735.2	36550
3	2790.7	35823	0	2734.3	36562
2	2790.2	35829	0	2733.5	36572
0	2789.4	35839	0	2732.1	36591
1	2788.1	35856	0	2730.0	36619
1	2786.6	35875	2	2727.5	36693
0	2786.2	35881	0	2721.9	36728
0	2781.4	35943	0	2719.5	36761
2	2780.7	35952	2	2714.3	36831
3	2780.0	35961	1	2706.8	36933*
4	2779.1	35972	1	2695.3	37091*
0	2778.2	35984	0	2683.8	37250*
0	2776.8	36002	0	2673.6	37392*
1	2770.0	36090	0	2666.8	37487*

(a) The bands marked \* are diffuse and about 50–60  $\text{cm}^{-1}$  in width and are therefore not included in the vibrational analysis. The wavelengths given represent the centres of the diffuse bands. On the short wavelength side of these diffuse bands there is the weak system 2660–2590 Å.

(b) The region 2810–2835 Å was found to consist of some traces of the rotational lines of the OH band. If this OH is eliminated one may find a few more bands than those recorded.

(c) The weak bands at 34364  $\text{cm}^{-1}$ , 35598  $\text{cm}^{-1}$  and 35704  $\text{cm}^{-1}$  can be represented by ( $v' = 16$ ,  $v'' = 38$ ), ( $v' = 17$ ,  $v'' = 19$ ) and ( $v' = 18$  and  $v'' = 19$ ) respectively. These are not included in Table II because to represent these bands the vibrational analysis has to be extended and a number of bands are to be repeated for this extension.

by more than  $1 \text{ cm.}^{-1}$  from the mean value, it is expected that there might be an error of 3 or  $4 \text{ cm.}^{-1}$  in the determination of the exact position of the band heads as the neighbouring bands in many cases were found to overlap with one another.

#### VIBRATIONAL ANALYSIS OF THE BAND SYSTEM 2950-2670

The vibrational scheme of the band system is shown in Table II and the intensity distribution in Table III. The Franck-Condon parabola that one gets is exactly of the form that one expects for the transition involving the observed  $\omega_0'$  and  $\omega_0''$  values.

The vibrational analysis shows that all the bands in the system could be well represented as involving a transition from an upper initial state at  $51802 \text{ cm.}^{-1}$  to the lower state at  $15918 \text{ cm.}^{-1}$  with the same  $\Delta G''(v + \frac{1}{2})$  values as given by Darbyshire<sup>17</sup> and Brown.<sup>18</sup> The lower state is the  ${}^3\Pi_u(O_u^+)$  state which forms the upper state of the visible absorption band system in the region  $8672\text{--}5110 \text{ \AA}$ .

The  $\Delta G''(v + \frac{1}{2})$  and  $\Delta G'(v + \frac{1}{2})$  values as obtained from the analysis are also shown in Table II. The  $\Delta G(v + \frac{1}{2})$  values for the  ${}^3\Pi_u(O_u^+)$  level obtained by Darbyshire and Brown from the studies of the visible absorption band system are also included in the table for comparison. Darbyshire from the analysis of the visible absorption band system indicated the existence of the perturbation of the levels  $v = 3$  and  $v = 4$  of the  ${}^3\Pi_u(O_u^+)$  state and the analysis of the present system confirms his observation. Because of this perturbation a single formula of the usual type cannot express accurately the positions of all the band heads in the system. But the vibrational constants  $\omega_0''$ ,  $\omega_0''x_0''$  and  $\omega_0'$ ,  $\omega_0'x_0'$  could be determined fairly accurately by the usual procedure from the observed  $\Delta G''(v + \frac{1}{2})$  and  $\Delta G'(v + \frac{1}{2})$  values. Since the  $\Delta G''(v + \frac{1}{2})$  values are practically the same as those obtained by Darbyshire and Brown, it was found that they could be fairly well represented with the vibrational constants  $\omega_0'' = 166.1 \text{ cm.}^{-1}$  and  $\omega_0''x_0'' = 1.84 \text{ cm.}^{-1}$  given by Darbyshire.<sup>17</sup> The  $\Delta G'(v + \frac{1}{2})$  values could be fairly well represented with the constants  $\omega_0' = 149.2 \text{ cm.}^{-1}$  and  $\omega_0'x_0' = 1.15 \text{ cm.}^{-1}$ . The  $\Delta G'(v + \frac{1}{2})$  values calculated with these constants are included in Table II for comparison.

#### ISOTOPIC SHIFTS

The three isotopic species of the bromine molecule are  $\text{Br}^{79}\text{Br}^{79}$ ,  $\text{Br}^{79}\text{Br}^{81}$ , and  $\text{Br}^{81}\text{Br}^{81}$  with an abundance ratio of 1:2:1 and therefore each band corresponding to the more abundant  $\text{Br}^{79}\text{Br}^{81}$  molecule is expected to have one weak band on the low frequency side and one weak band on the high





frequency side. The vibrational analysis given in Table II corresponds to the molecule  $\text{Br}^{79}\text{Br}^{81}$ . The calculated and the probable observed isotopic shifts for some of the strong bands, which could be recognized, are shown in Table IV. For the remaining strong bands the isotopic shifts are either expected to be

TABLE IV  
*Isotopic shifts of some bands in the system 2950–2670 Å*

$v', v''$	$\nu$ in $\text{cm.}^{-1}$	I	$\Delta\nu_{obs.}$ $\text{cm.}^{-1}$	$\Delta\nu_{calc.}$ $\text{cm.}^{-1}$
8, 27	33860	1	5.5	3.8
	33866	2		
	33871	1		
1, 15	33941	1	7.0	9.3
	33948	2		
	33955	0		
9, 27	33996	0	4.0	3.1
	33999	1		
	34004	0		
8, 25	34008	2	5.5	4.6
	34013	3		
	34019	0		
8, 24	34084	1	5.5	4.7
	34088	5		
	34095	1		
3, 16	34128	5	7.0	9
	34135	6		
	34142	0		
1, 13	34187	9	7.0	8.5
	34194	7		
3, 15	34228	5	8.5	7.6
	34237	8		
	34245	5		
4, 16	34278	4	6.0	7.1
	34284	0		
1, 12	34304	10	9.0	8.1
	34313	1		

TABLE IV—(Contd.)

$v', v''$	$\nu$ in $\text{cm.}^{-1}$	I	$\Delta_{\text{obs. cm.}^{-1}}$	$\Delta\nu_{\text{calc. cm.}^{-1}}$
5, 17	34304	10	4.5	6.4
	34308	10		
	34313	1		
4, 15	34378	5	8.0	6.8
	34386	5		
0, 10	34411	3	8.0	8.5
	34419	6		
1, 11	34419	6	6.5	7.6
	34425	6		
	34432	3		
4, 14	34480	4	6.0	6.5
	34487	4		
	34492	0		
6, 16	34541	2	6.0	5.5
	34548	7		
	34553	0		
2, 11	34565	0	5.0	6.7
	34569	3		
	34575	0		
7, 16	34690	7	4.0	4.8
	34693	7		
	34698	2		
1, 7	34951	3	8.5	5.2
	34958	3		
	34968	3		
0, 6	34951	3	7.0	5.8
	34958	3		
2, 8	34968	3	5.0	5.0
	34973	0		
0, 5	35102	5	5.0	4.9
	35107	4		
2, 6	35253	5	4.0	3.5
	35257	2		

less than  $2 \text{ cm.}^{-1}$  or are probably overlapped by the neighbouring bands and, therefore, could not be measured.† It is to be noted that a number of the bands which could be represented as belonging to  $\text{Br}^{79}\text{Br}^{79}$  or  $\text{Br}^{81}\text{Br}^{81}$ , could also be represented as belonging to  $\text{Br}^{79}\text{Br}^{81}$  with different  $v'$ ,  $v''$  values and therefore also included as such in Table II. This may be the reason why the expected ratio of the relative intensities among the three bands belonging to three isotopic species is not maintained. For some of the bands, isotopic shifts on the short wavelength side only could be observed. The one on the long wavelength side is probably masked by the main band ( $\text{Br}^{79}\text{Br}^{81}$ ) which is degraded to longer wavelengths. Agreement between the calculated and the probable observed isotopic shifts supports the correctness of the vibrational analysis given.

#### THE ELECTRONIC TRANSITION INVOLVED

As stated earlier, the lower state of the system is the  ${}^3\Pi_u(\text{O}_u^+)$  level with the configuration  $\sigma_g^2\pi_u^4\pi_g^3\sigma_u$ . As regards the upper state it is difficult to say definitely which electronic state is involved, unless the rotational structure of the bands is studied. The second order plates and a fourth order plate tried for the strong portion of the spectrum could only show partially resolved structure. It is expected that it would probably be easy to obtain the rotational structure of the analogous system‡ in chlorine and decide about the upper electronic term involved.

However, with the help of the term scheme developed by Mulliken<sup>20</sup> for iodine molecule and later extended by Asundi and Venkateswarlu<sup>6</sup> to bromine molecule one can see that the only configuration that is expected to give "gerade" states around  $50,000 \text{ cm.}^{-1}$  is  $\sigma_g^2\pi_u^2\pi_g^4\sigma_u^2$ . This configuration gives the states  ${}^1\Sigma_g^+(\text{O}_g^+)$ ,  ${}^3\Sigma_g^-(\text{O}_g^+, 1_g)$  and  ${}^1\Delta_g(2_g)$ , of which the last cannot combine with the  ${}^3\Pi_u(\text{O}_u^+)$  state as the coupling is expected

† It is probably because of similar reasons that only few isotopic displacements were measured by earlier workers,<sup>18, 17</sup> in the absorption band systems of bromine in the visible and near infra-red regions. Brown<sup>18</sup> recorded isotopic shifts for only 18 bands out of a total number of 90 bands put by him in the Deslandres scheme for the visible absorption band system (6950–5110 Å). Darbyshire<sup>17</sup> extended the system upto 8672 Å and arranged 22 new bands in the extension of the Deslandres scheme, but could measure only twelve possible isotopic displacements of which he was sure six to be free from overlapping of other bands. Similarly in the system 6450–8150 Å he could measure only three isotopic displacements.

‡ Cameron and Elliott<sup>15</sup> excited chlorine in presence of active nitrogen and obtained a set of closely spaced bands in the region 2580–2380 Å where only two continua show up with the intensity maxima at 2565 Å and 2430 Å, if chlorine is excited electrically<sup>21, 22</sup> without the presence of a foreign gas. They gave the wavelengths of these bands as obtained with a medium quartz spectrograph. The wave number separation of the bands in the progressions suggests that the band system probably involves the  ${}^3\Pi_u(\text{O}_u^+)$  state and therefore, is analogous to the present band system of bromine. Further work on this chlorine system is in progress in this laboratory.

to be nearer to that of Hund's case (c). The calculated average position of the states that arise from  $\sigma_g^2\pi_u^2\pi_g^4\sigma_u^2$  is 6.0 ev. and  $^1\Sigma_g^+(\text{O}_g^+)$  is expected to be higher than  $^3\Sigma_g^-(\text{O}_g^+, 1_g)$ . The position of the upper state of the present band system is at 51802  $\text{cm}^{-1}$  or 6.4 ev. and one can therefore tentatively assign  $^1\Sigma_g^+(\text{O}_g^+)$  to this state. The presence of the two strongly antibonding electrons explains the low value of the vibrational frequency of the state which is less than half of the ground state. The probable ionic character predicted by Mulliken<sup>20</sup> for this state suggests a high value for the dissociation energy§ of this state.

#### THE EFFECT OF THE FOREIGN GAS

When bromine is excited without the presence of argon gas, the region 2980–2680 Å shows two groups of diffuse bands. The first group consists of six diffuse bands with the most intense one at 2900 Å, while the second group consists of five diffuse bands with the most intense one at 2754 Å. Unless the spectrum is taken on plates showing good contrast, these groups of diffuse bands appear as two continua with maxima at 2900 Å and 2754 Å respectively. The average separation of the constituent bands in both the groups is of the order of 330  $\text{cm}^{-1}$ . Venkateswarlu<sup>5</sup> explained these two groups of bands along with others as arising in an upper stable *gerade* electronic state at about 55534  $\text{cm}^{-1}$  and having for the final levels two unstable *ungerade* states dissociating into  $^2\text{P}_{3/2} + ^2\text{P}_{1/2}$  bromine atoms. The mutual separation of the diffuse bands gave the frequency of the upper state. It appears that when bromine is excited electrically, the electronic state at 55534  $\text{cm}^{-1}$  which has the same  $r_e$  value as the ground state, is very easily reached and groups of intense diffuse bands occur because of transitions to

§ It may be pointed out that the linear extrapolation method using the values  $\omega_0' = 149.35 \text{ cm}^{-1}$  and  $\omega_0'x_0' = 1.15 \text{ cm}^{-1}$  gives  $D_0 = 4849 \text{ cm}^{-1}$  and  $D_0 = 4924 \text{ cm}^{-1}$  for the dissociation energy of the state which will then have the dissociation limit at 56726  $\text{cm}^{-1}$ . This value can be seen to be much lower than the levels of the lowest possible dissociation products. This anomaly can be understood if one considers this state to be an ionic state and remembers as pointed out by Gaydon<sup>23</sup> that the linear extrapolation method cannot be used to obtain the dissociation energy of the ionic state as it was found in many cases to give values very much lower than the correct ones. It is to be noted further that the  $\Delta G'(v + \frac{1}{2})$  values are observed only upto  $v' = 15$  and it is too much to attempt to find the dissociation energy of this state with these few  $\Delta G'(v + \frac{1}{2})$  values. However, it can be pointed out that the last two observed  $\Delta G'(v + \frac{1}{2})$  values indicate the existence of a positive cubic term ( $\omega_0 y_0 v^3$ ) which will, of course, take up the dissociation limit to higher values. It will always be possible to adjust the higher order terms in such a way that the calculated values agree well with the few observed  $\Delta G'(v + \frac{1}{2})$  values and at the same time give as much high dissociation energy as we want. For instance the vibrational constants  $\omega_0' = 149.35 \text{ cm}^{-1}$ ,  $\omega_0'x_0' = 1.25 \text{ cm}^{-1}$ ,  $\omega_0'y_0' = 0.01 \text{ cm}^{-1}$  and  $\omega_0'z_0' = 0.00003 \text{ cm}^{-1}$  give  $\Delta G'(v + \frac{1}{2})$  values in agreement with those observed and give a dissociation energy of about 14,000  $\text{cm}^{-1}$ .

different repulsive states. When the foreign gas is introduced, collisions take place and the molecule is taken away from the stable state at  $55534\text{ cm.}^{-1}$  to the different vibrational levels of the stable state at  $51802\text{ cm.}^{-1}$  having smaller  $\omega_e$  value and therefore larger  $r_e$  value. Transition then takes place from this state to the  ${}^3\Pi_u(\text{O}_u^+)$  state at  $15918\text{ cm.}^{-1}$  which has also a large  $r_e$  value. As one increases the pressure of the argon gas, more molecules reach the state at  $51802\text{ cm.}^{-1}$  by collisions and the discrete band system  $2950\text{--}2670\text{ \AA}$  increases in intensity while the group of diffuse bands in the region decrease in intensity.

#### FURTHER REMARKS

At  $940^\circ\text{ C.}$  and  $270\text{ mm.}$  pressure of bromine Dabrowski<sup>24</sup> obtained in absorption a weak band near  $2930\text{ \AA}$  with a sharp limit on the long wavelength side. This absorption may probably correspond to the first group of the overlapping diffuse bands mentioned above in emission. The occurrence of this absorption at high temperature can be explained as a transition from the repulsive state reached by the recombination of the  ${}^2\text{P}_{3/2} + {}^2\text{P}_{1/2}$  bromine atoms to the upper stable state at  $55534\text{ cm.}^{-1}$ , the bromine atoms having been probably obtained by thermal dissociation of molecules at high temperature. This view is supported by the fact that at high temperatures Uchida<sup>16</sup> obtained in thermal luminescence a discrete band system in the visible region which is completely identical with the visible absorption band system and which can be explained only on the basis that the initial state  ${}^3\Pi_u(\text{O}_u^+)$  of the system is formed by the recombination of  ${}^2\text{P}_{3/2} + {}^2\text{P}_{1/2}$  bromine atoms.

This absorption along with that of Dabrowski incidentally suggests that the band system  $2950\text{--}2670\text{ \AA}$  discussed in the present paper may be observed in absorption at high temperatures if proper conditions of temperature and pressure are reached. The intensity of this system in absorption will, of course, depend upon the life-time of the molecules in the  ${}^3\Pi_u(\text{O}_u^+)$  state.

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## REFERENCES

1. Uchida, Y. and Ota, Y. .. *Jap. Jour. Phys. (Tokyo)*, 1928, **5**, 59.
2. Haranath, P. B. V. and Rao, P. T. .. *Ind. Jour. Phys.*, 1955, **29**, 205.
3. Strutt, R. J. and Fowler, A. .. *Proc. Roy. Soc. (London)*, 1912, **86 A**, 105.
4. Ludlam, B. and West, W. .. *Ibid., Edinburgh*, 1923-24, **44**, 85.
5. Venkateswarlu, P. .. *Proc. Ind. Acad. Sci.*, 1947, **25**, 138.
6. Asundi, R. K. and Venkateswarlu, P. .. *Ind. Jour. Phys.*, 1947, **21**, 101.
7. Herzberg, G. .. *Spectra of Diatomic Molecules*, D. Van Nostrand Company, New York, 1950.
8. Asagoe, K. and Inuzuka, Y. .. *Sci. Rep. Tokyo Burnika Daigaku*, 1934, **2 A**, 73.
9. Venkateswarlu, P. .. *Proc. Ind. Acad. Sci.*, 1946, **24 A**, 480;  
*Ibid.*, 1947, **25 A**, 119 and 133.  
(Earlier references on Iodine are given in these papers.)
10. Oldenburg, O. .. *Z. Physik.*, 1924, **25**, 135.
11. Duchinsky, F. and Pringsheim, P. .. *Physica*, 1935, **2**, 923.
12. Elliott, A. .. *Proc. Roy. Soc. (London)*, 1940, **174 A**, 273.
13. Waser, J. and Wieland, K. .. *Nature*, 1947, **160**, 643.
14. Venkateswarlu, P. .. *Phys. Rev.*, 1951, **81**, 821.
15. Cameron, W. H. B. and Elliott, A. .. *Proc. Roy. Soc. (London)*, 1938-39, **169 A**, 463. (See Footnote on p. 465 of this article.)
16. Uchida, Y. .. *Sci. Papers Inst. Phys. Chem. Res.*, 1936, **30**, 71.
17. Darbyshire, O. .. *Proc. Roy. Soc. (London)*, 1937, **159**, 93.
18. Brown, W. G. .. *Phys. Rev.*, 1931, **38**, 1179-86.
19. ——— .. *Ibid.*, 1932, **39**, 777-87.
20. Mullikan, R. S. .. *Ibid.*, 1934, **46**, 549.
21. Elliott, A. and Cameron, W. H. B. .. *Proc. Roy. Soc. (London)*, 1937, **158 A**, 681.
22. Venkateswarlu, P. .. *Proc. Ind. Acad. Sci.*, 1947, **26 A**, 22.
23. Gaydon, A. G. .. *Dissociation Energies and Spectra of Diatomic Molecules*, Chapman and Hall Ltd., London, 1947.
24. Dabrowski, L. .. *Acta Physica Polonica*, 1934, **3**, 301.

EXPLANATION OF PLATES  
PLATES X AND XI

Fig. 1. (a), (b) & (c) Enlargements of the band system 2950-2670 Å of bromine photographed in the 1st order of 21 ft. grating spectrograph.

(d) Extra enlargement of the band system 2950-2670 Å in the region 2940-2830 Å showing bipbaroe isotopic shifts.