

## BAND SPECTRUM OF ZINC BROMIDE.

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### INTRODUCTION.

The band spectrum of the molecule of Zinc Bromide is the least known of the halides of Zinc. The only reported bands in the literature are those obtained by Walter and Barratt (1929) in absorption, 17 of them being measured from 3113Å to 3027Å. Howell (1943) examined these bands in the light of his argument that the spectra of Zinc halides, resulting from the excitation of the Zn 4s electron, should be due to a  ${}^2\pi - {}^2\Sigma$  transition in which the  ${}^2\pi$  separation is  $2/3(4p, {}^3P, \text{Zn}) = 386 \text{ cm.}^{-1}$ . Taking the two strongest of the Walter and Barratt absorption bands at  $\lambda 3071$ ,  $\nu 32553$  and  $\lambda 3110$ ,  $\nu 32145$  as the (0, 0) bands of the two component systems of the  ${}^2\pi - {}^2\Sigma$  transition, he suggested a vibrational analysis.

Howell considered that the intensity distribution among the bands was in complete support of the proposed scheme and approximate values of  $\omega'$  and  $\omega''$  were derived to be 250 and 220 units respectively, but an unexpected difficulty arose when the ZnI bands are considered. The magnitude of the lower state vibrational frequency, i.e., 220  $\text{cm.}^{-1}$  is almost nearly equal to the corresponding well-established constant of the ZnI molecule. Howell was hence led to suspect the origin of the Walter and Barratt absorption bands and only tentatively assigned them to the ZnBr molecule indicating an obvious need for further work.

### EXPERIMENTAL.

The authors investigated the spectrum of Zinc Bromide in emission under the conditions found suitable for the excitation of the other allied halides. Chemically pure Zinc Bromide is taken in a Pyrex discharge tube of simplified design (Ramasastry and K. R. Rao (1947); Ramasastry, 1948) and its characteristic spectrum is excited by a high frequency voltage (about 150v, 8Mc.) applied to the tube by means of external electrodes. As the molecule responsible for the Walter and Barratt's absorption bands was somewhat of a doubtful nature, the experiments are repeated with two samples of Zinc Bromide, one the post-war B.D.H. product and the other a prewar Merck supply. In both cases the spectra obtained were identical. Preliminary work with Hilger Medium quartz instrument showed that the entire spectrum from 2000Å to 6500Å consisted of only two groups of bands, one in the near ultraviolet round about 3000Å and the other in the visible. Due to the presence of many atomic lines of Zinc in the 3050Å region, the first group of bands are difficult to be identified at first glance as some of them appear line-like in the low dispersion. This difficulty is, however, got over to a large extent by giving a Zinc arc comparison also in juxtaposition with the ZnBr spectrum. Littrow quartz spectrograms brought out more clearly the existence of these bands.

#### *Near Ultraviolet Bands of Zinc Bromide Systems C and D.*

These emission bands are obtained for the first time in the present work. Table I contains the wavelength data. The absorption measurements of Walter

TABLE I.

*Near Ultraviolet Bands of Zinc Bromide.*

Band Head Data.				Assignment.				Remarks.
Walter and Barratt (Absorption).		Authors (Emission).		Authors.		Howell.		
$\lambda$ (Int.)	$\nu$	$\lambda$ (Int.)	$\nu$	System	Head type.	System	Head type.	
3113(1)	32114	3111-6(3)	32128	C(1, 1)	Q	C(0, 0)	P	Zn line also. Violet degraded. Zn line also.
3110(4)	32145	3111-6(3)	32143	C(1, 1)	R	C(0, 0)	Q	
		3108-9(5)	32157	C(0, 0)	Q			
		3107-6(4)	32170	C(0, 0)	R			
3102(2)	32228	3102-3(1)	32224	D(0, 1)		C(1, 1)		
3093(1)	32322			D(2, 3)		C(2, 2)		
3085(1)	32405			D(4, 5)		C(3, 3)		
		3081-7(4)	32440	C(1, 0)				
		3075-8(-)	32502					
		3072-8(2)	32535	D(0, 0)	P			
3071(4)	32553	3072-0(5)	32542	D(0, 0)	Q	D(0, 0)		
3068(3)	32585			D(1, 1)		D(1, 1)		
3064(2)	32628			D(2, 2)		D(2, 2)		
3060(1)	32670	3059-6 (0bd)	32675	D(3, 3)		D(3, 3)		
3056(0)	32713	3055-8(8d)	32715	C(2, 0) and D(4, 4)		D(4, 4)		
		3053-3(0)	32742					
3052(0)	32756	3051-7(0)	32760	D(5, 5)		D(5, 5)		
		3049-8(0)	32779(M)					
3048(0)	32799			D(6, 6)		D(0, 1)		
3044(0)	32842			D(7, 7)		D(1, 2)		
3039(0)	32896			D(1, 0)		D(2, 3)		
3035(0)	32939	3035-8(?)	32931	D(2, 1)		D(3, 4)		
		3034-8(1)	32942					
3031(00)	32963			D(3, 2)		D(4, 5)		
		3030-2(5)	32991	C(3, 0)				
		3027-9(0)	33017					
		3027-5(0)	33022					
3027(00)	33026	3027-0(0)	33027	D(4, 3)		D(5, 6)	Components.	
		3023-1(1)	33069(M)	D(5, 4)				
		3018-3(?)	33122(M)				Masked by Zn line.	
		3017-3(1)	33133(M)					
		3013-7(0)	33172					
		3013-2(1)	33177				Components.	
		3012-9(1)	33180					
		3012-4(1)	33186					
		3005-0(2)	33268(M)	C(4, 0)				
		3002-1(1)	33300(M)					
		2997-8(1)	33348(M)					
		2989-9(2)	33436(M)					
		2983-8(1)	33505(M)				Isotopic heads?	
		2982-4(1)	33520(M)					
		2966-5(2)	33700(M)					

Note—Wavenumbers marked (M) are those measured only on the Medium Quartz Spectrograms.

and Barratt are also given in the same table. It could be seen that certain bands obtained in emission are not recorded in absorption and vice versa. In obtaining the vibrational analysis of these bands the following points of view are chiefly considered.

1. The assignment of the bands to the ZnBr molecule is supported by the authors' experimental results.

2. Examination of the relative values of the constants of Zinc halides shows that  $\omega_e'' = 220$ , derived by Howell for the lower state of ZnBr is certainly too small. The upper state constant  $\omega_e' = 250$  is also out of step in the sequence of values of the constants of the corresponding states of the other Zinc halides (cf. Table II).

TABLE II.

*Constants of the Band systems of Zinc Halides occurring near the  $3P-1S$  Zn lines.*

Molecule.	(0, 0) Band.	$\Delta\nu$	$\omega_e'$	$\omega_e''$	Reference.
ZnF	2677.0, 37344 2703.8, 36934	370	597 601	620 620	Rochester and Olsson (1939).
ZnCl	2942.2, 33978 2975.9, 33593	385	382 384	391 390	Cornell (1938).
ZnBr	3072.8, 32542 3108.9, 32157	386	$\sim 358$ $\sim 284$	$\sim 318$ $\sim 312$	Present work.*
	3071 , 32553 3110 , 32145	408	$\sim 250$ ..	$\sim 220$ ..	Howell (1943).
ZnI	3277.8, 30499 3318.1, 30129	370	$\sim 212$ 248	$\sim 220$ 223	Tiruvenganna Rao and K. R. Rao (1946). Howell (1943).

\* From the new analysis given in the following pages.

3. The band system occurs in the region expected for the Zinc Bromide molecule and the electronic width of  $408 \text{ cm.}^{-1}$  deduced by Howell is of the correct order of magnitude.

4. The ground state vibrational frequency of ZnBr should lie between 390 of ZnCl and 223 of ZnI. This range could further be narrowed down (Ramasastry, 1949) as this constant should have a value intermediate between those of CuBr ( $\omega_e'' = 314$ ) and GaBr ( $\omega_e'' = 263$ ).

5. Two component systems of  $2\pi-2\Sigma$  transition should occur and the main difficulty in the analysis is presumed to have arisen from the overlapping of the two component systems.

Strips (a) and (b) of Plate XIV are the enlargements of these bands from the Medium and Littrow Quartz spectrograms respectively. These consist of (1) a group of four headless bands in the  $3110\text{\AA}$  region, (2) a definitely violet degraded band at  $3072\text{\AA}$  with a weak P-head accompanying it, (3) a few other diffuse bands, some of these showed four components when seen under high magnification. Considering the band at  $\lambda 3072$ ,  $\nu 32542$  as the (0, 0) of one component system and the intense head at  $\lambda 3108.9$ ,  $\nu 32157$  of the  $3110$  group as the (0, 0) band of the other component system, the separation between the (0, 0) bands is obtained as  $386 \text{ cm.}^{-1}$  which agrees well with the predicted  $2\pi$  width of  $386 \text{ cm.}^{-1}$ . On this basis, the four bands of the  $3110$  group are to be interpreted as R and Q heads of the (0, 0) and (1, 1) bands. This interpretation and the presence of a weak P-head accompanying the band at  $3072\text{\AA}$  are consistent with the  $2\pi-2\Sigma$  transition.

The diffuse bands, present on the plate, form into a regular progression with the (0, 0) band at  $3108.8\text{\AA}$ ,  $\nu 32157$  as the first member. The vibrational scheme is shown in Table I. This component system of the  $2\pi-2\Sigma$  transition is designated as system C in conformity with the designations of the band systems of the other related molecules. The lower state frequency is about  $312\text{ cm.}^{-1}$  which is of the correct order of magnitude. The component heads observed in the diffuse bands may be of isotopic origin.

*System D.*

The faint band at  $\lambda 3102.3$ ,  $\nu 32224$  may now be considered as the (1, 1) band of the second component system (hereafter referred to as system D), giving a lower state  $\omega$  value of about  $318\text{ cm.}^{-1}$ , with the (0, 0) band at  $\lambda 3072.0$ ,  $\nu 32542$ . Thus this system consists of only these two bands in emission.

Intensity considerations, namely that one of the component systems of the  $2\pi-2\Sigma$  transition is poorly developed in the case of the other halides of Zn, Cd and Hg, also support this analysis. Further, the bands obtained by Walter and Barratt in absorption but not recorded in emission in the present work could also be fitted into the above analysis. The new classification of the Walter and Barratt absorption data is shown in Table I together with that of Howell.

Of the two components of the  $2\pi-2\Sigma$  transition, one is developed better in absorption and the other better in emission. The absorption and emission data are chiefly complementary; there are of course a few common bands. The vibrational constants for both the component systems and the  $2\pi$  electronic width are of the correct order of magnitude.

It has not been possible to include in the above analysis some of the diffuse bands occurring at the short wavelength end. It may be significant to note that about five bands starting with  $\nu 33180$  are approximately equally spaced at intervals of about  $83\text{ cm.}^{-1}$  and as, in all probability, these bands also belong to ZnBr, they may form another system altogether different from the two component band systems C and D of the  $2\pi-2\Sigma$  transition. There is need here for further investigation; particularly absorption pictures may prove to be of considerable help.

TABLE III.  
*Band Head data of Visible Bands of ZnBr.*

Wavelength.	Int.	Wavenumber.	Wavelength.	Int.	Wavenumber.
4253.0	1	23506	3924.0	2	25477
30.0	1	23634	04.0	2	25608
04.0	1	23780			
			3885.5	2	25729
4181.5	1	23908	65.0	3	25866
60.5	1	24029	46.5	3	25990
40.0	1	24148	26.0	2	26130
17.5	1	24280	07.5	3	26257
4093.5	1	24422	3789.0	2	26385
70.5	1	24560	71.0	2	26511
49.0	1	24691	52.5	1	26641
28.0	2	24819	35.0	1	26766
06.0	2	24956	17.0	1	26896
3988.0	2	25068	3699.0	1	27027
66.0	2	25207	80.5	1	27163
45.5	2	25338	64.0	1	27264

*The 'Visible' Bands.*

The visible bands obtained in the present work extend from  $4500\text{\AA}$ – $3600\text{\AA}$ . They are reproduced in strip (c). The direction of degradation is clearly towards the red but owing to the weak intensity of the bands and a general continuum covering them up, there is not much of contrast and consequently about 30 band heads only could be measured on the Hilger Medium Quartz and Fuess Glass spectrograms. The heads are not quite sharp excepting a few individual cases near  $3850\text{\AA}$  and the measurements which may be correct to an Angstrom unit are given in Table III.

The band heads are located at approximately equal intervals of  $130\text{ cm.}^{-1}$ . Some of these bands showed partial resolution of rotational structure under the higher dispersion of the  $E_1$  spectrograph. These 'visible bands' of ZnBr resemble, in their appearance, those of CdCl (Ramasastry, 1947), CdBr (Ramasastry, 1949) and ZnCl (from unpublished results of this laboratory), while the 'visible bands' of HgCl, HgBr, HgI, CdI, and ZnI have an altogether different appearance.

## SUMMARY.

The characteristic emission band spectrum of Zinc Bromide molecule is recorded for the first time and it is found to consist of mainly two groups of bands, one in the near ultraviolet from  $3110\text{\AA}$  to  $2980\text{\AA}$  and the other in the visible. The near ultraviolet bands appear like diffuse lines and are analysed into two component systems, C and D, of a  ${}^2\pi$ – ${}^2\Sigma$  electronic transition with a  ${}^2\pi$  width of  $386\text{ cm.}^{-1}$  and the following vibrational constants:

	(0, 0) band	$\omega_e''$	$\omega_e'$
System C	32157	$\sim 312$	$\sim 280$
System D	32542	$\sim 318$	$\sim 350$

The absorption data of Walter and Barratt could easily be fitted into the above analysis. The emission data (present work) and the absorption data (Walter and Barratt) are chiefly complementary; there are of course a few common bands.

Measurements of about 30 red-degraded bands of ZnBr from  $4500\text{\AA}$  to  $3600\text{\AA}$  are also given and a recurring interval of 130 or  $260\text{ cm.}^{-1}$  is indicated.

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