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THE EMISSION SPECTRUM OF BROMINE

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Plates V A-B

ABSTRACT. The emission spectrum of bromine as excited by a high frequency high power oscillator is photographed in the visible region, λ 6400 to λ 4400 and is found to consist of as many as 300 bands as against only 80 bands reported previously by Uchida and Ota in the region λ 6700 to λ 5000. Tentative vibrational analysis of the bands on the basis of two systems suggested by Uchida and Ota are considerably extended to include all the bands down to λ 4400. This has led to a redetermination of the following vibrational constants

	ω'_e	$x'_e\omega'_e$	ω''_e	$x''_e\omega''_e$	ν_e
System I	190.0	1.0	376.0	1.25	19290.0
System II	152.0	0.35	376.0	1.25	18782.0

The vibrational assignments are well supported by an extensive study of the bromine isotope effect.

INTRODUCTION

The emission spectra of chlorine and bromine in the visible region are well known. Uchida and Ota (to be referred to as UO) (1928) first reported three systems in the emission spectrum of chlorine. Later Elliot and Cameron (1938) reinvestigated these bands and offered a different analysis from the one proposed earlier by UO, on the basis of two systems ascribed to the transition $^2\Pi - {}^2\Pi$. From the even multiplicity of the systems involved they considered that the emitting molecule may be the ionised molecule Cl_2^+. In view of the uncertainty in the analysis proposed earlier and the number of systems involved in the spectrum of C_2^+, Howell (1953) suggests that the main difficulty in the analysis of the emission bands of Cl_2^+ is due to the fact that the $^2\Pi$ separaration of the ground state is of the same order of magnitude as the ground state vibrational frequency. Hence he concludes that a study of the spectrum of Br_2^+ would be more helpful in determining the nature of electronic levels and the relative order of values of ω_e' and ω_e''. In the light of this suggestion it is considered worthwhile to undertake a detailed study of the emission band spectrum of bromine.

UO (1928) were the first to suggest the vibrational analyses of the emission bands of bromine in the region λ 6700 – λ 5000 as belonging to two systems. The following vibrational quantum formulae were derived from the analyses.

System I $\quad \nu = 17325.80+191.45n'-1.05n'^2-360.65n''+0.65n''^2$

System II $\quad \nu = 16105.00+152.40n'-0.40n'^2-361.70n''+1.62n''^2$

It is noteworthy that the intensity distribution in both the systems is of the open Franck-Condon parabola type which is normally to be expected for such divergent values of ω_e' and ω_e''. However, they admit that the quantum numbering of the bands is quite arbitrary as the assignments were not supported by bromine isotope effect. The bands in these two systems, as in the case of chlorine, bear no relationship with absorption bands of the neutral bromine molecule. The present paper describes the results of the authors obtained on the emission spectrum of bormine which is found to consist of as many as 300 bands in the region λ6700 down to λ4400.

EXPERIMENTAL

UO excited the spectrum through an induction coil discharge generating bromine by heating silver bromide. In the present work the spectrum of bromine was excited in an electrodeless discharge from a high frequency high power oscillator. For photographing the bands a pure sample of cupric bromide was spread uniformly in the middle of the tube. The discharge tube was made of pyrex glass of length 30 cm and diameter 1.6 cm and was drawn into an adopter at one end for evacuation by a Cenco Hyvac pump. The other end was fitted with a glass window by means of shellac. The heat of the electrodes was found sufficient to maintain a steady column of bromine vapour. The discharge which appears rose-red in colour could be maintained for several hours free from any traces of either the usual impurity bands or those of CuBr. The design of the discharge tube was slightly altered when the spectrum was excited using pure fuming liquid bromine. In this case the tube having the same diameter was closed at one end and was provided with two side limbs to one of which was connected a small bulb containing pure liquid bromine. The pressure of bromine inside the discharge tube was regulated by adjusting a pinch-cock attached to the pressure tubing connecting the bromine container to the discharge tube. The other limb was connected to a Cenco Hyvac pump through a liquid air trap. It was found that at some optimum pressure the development of the spectrum was more satisfactory than in the case of cupric bromide.

Photographs of the spectra were taken both on Fuess and three-prism glass Littrow spectrographs, using Ilford Special Rapid panchromatic plates. Exposures varying from one to two hours were found necessary to obtain the bands on the Fuess instrument while longer exposures of six hours were necessary on the Littrow instrument. The development of the spectrum which extends from λ6400—λ4400 was found to be better in the region below λ5000 in the Fuess spectrograms. Hence measurements of band heads in the region λ6400 to λ5000 were made on Littrow plates and below 5000 on Fuess plates. A number of plates were measured and the mean wavelengths were deduced using international iron arc tandards. Measurements on different plates seldom differ by more than two wave number units. Table I records the band head data and assignments.

TABLE I

Authors		Uchida, Ota, Wave-number	Int	Assignment	
Wave-length	Wave-number			System I v',v''	System II v',v''
6604.1		15137.9			3,11
6579.0		15195.7			
6540.7		15284.6			4,11
6519.7		15333.9			2,10
6499.6		15381.7		1,11	0,9
6476.6		15435.9			5,11
6455.1		15487.3			3,10
6435.9		15533.5			1,9
6421.2		15569.1		2,11	
6413.7		15587.3		4,12	6,11
6403.0		15613.3			
6392.8		15638.2			4,10
6372.1		15689.0			2,9
6366.8	15702i		1		
6357.5	15725	15725.1	2	1,10	
6343.4	15760		1	3,11	
6338.1	15773		1	5,12	
6333.0	15786	15786.4	2		5,10
6314.8	15831	15829.9	0		
6310.5	15842	15841.9	2		3,9
6299.5	15870		1		
6290.0	15894	15893.6	2	0,9	
6282.2	15914	15914.1	3	2,10	
6273.6	15935	15935.1	4	4,11	6,10
6268.1	15949	15949.1	2	6,12	
6259.1	15972i	15970.0	1		
6251.3	15992	15991.7	2		4,9
6244.7	16009i		1		
6225.5	16058i		1		
6217.3	16080	16080.4	4	1,9	7,10

TABLE 1 (*contd.*)

Authors		Uchida, Ota Wave-number	Int	Assignment	
Wave-length	Wave-number			System I v',v''	System II v',v''
6106.6	16107	16107.3	3	3,10	
6105.0	16112i		1		
6200.5	16123	16123.0	2	5,11	
6194.5	16139	16139.1	3		5,9
6188.0	16156i		1		
6182.5	16170	16172.0	0		
6152.1	16250		1	0,8	
6145.0	16269	16269.4	3	2,9	
6140.8	16280i		3		
6137.7	16288	16287.7	3	4,10	6,9
6133.3	16300	16300.4	4	6,11	
6127.0	16317i	16316.1	2		
6122.0	16330i		1		
6115.8	16347	16344.4	3		4,8
6110.1	16362i		2		
6089.1	16418i		3		
6083.2	16434	16434.4	8	1,8	7,9
6077.3	16450i		3		
6074.7	16457	16457.4	8	3,9	
6068.1	16475	16474.8	8	5,10	
6060.0	16497		4		5,8
6055.3	16510i		1		
6033.4	16570i		4		
6028.0	16585	16585.2	8		8,9
6021.7	16602i	16601.7	3		
6013.0	16626	16625.7	4	2,8	
6008.0	16641	16640.9	1		6,8
6004.7	16649	16649.2	4	4,9	
5999.1	16665		2		
5980.2	16716i		4		

TABLE I (*contd.*)

Authors		Uchida, Ota Wave-number	Int	Assignment	
Wave-length	Wave-number			System I v',v''	System II v',v''
5976.1	16729	16729.5	7		9,9
5972.4	16739i		4		
5959.4	16776i		4		
5954.5	16789		8		7,8
5950.0	16802i		4		
5945.7	16814	16814.2	4	3,8	
5940.8	16828	16828.3	4	5,9	
5935.4	16843		3		
5909.6	16917i		5		
5905.0	16930	16930.1	8		8,8
5901.2	16941i		5		
5891.1	16970		5		
5885.6	16986		4	2,7	
5879.7	17000	17000.3	6	6,9	6,7
5876.5	17012i		3		
5855.4	17073i		2		
5852.3	17083	17083.1	5		9,8
5848.7	17093i		3		
5830.2	17147		8		7,7
5826.5	17158i		5		
5821.2	17174	17178.2	6	3,7	
5818.3	17182		8	7,9	
5814.0	17195		2		
5804.6	17223	17223.2	4		10,8
5801.3	17233i		4		
5776.1	17308		2		
5770.4	17325		2		
5762.7	17348i		3		
5758.4	17361	17361.4	7	6,8	6,6
5754.7	17372i		2		

TABLE I (*contd.*)

Authors		Uchida, Ota Wave-number	Int.	Assignment	
Wave-length	Wave-number			System I v',v''	System II v',v''
5731.8	17442	17442.3	4		9,7
5728.6	17451i		2		
5711.3	17504i		2		
5708.7	17512		3		7,6
5703.6	17528		4	9,9	
5699.6	17540	17539.3		7,8	
5697.0	17548i		3		
5690.6	17568i		2		
5684.7	17586	17586.2	4		10,7
5679.0	17604i		2		
5666.4	17643		1		
5662.7	17654i	17650.5	2		
5660.0	17663		4		8,6
5657.7	17670i		2		
5644.9	17710	17710.8	4	8,8	
5642.2	17718	17718.6	5	6,7	
5639.9	17726i		3		
5620.2	17788		1		
5615.3	17804		2		9,6
5602.0	17846		3		
5594.2	17871		4		7,5
5589.4	17886		3	9,8	
5586.0	17897	17896.6	5	7,7	
5583.2	17906		2	5,6	
5575.2	17932		0		
5571.4	17944		1		10,6
5548.1	18019		1		8,5
5543.3	18035		1		
5532.5	18070	18070.3	1	8,7	
5529.1	18081	18080.7	1	6,6	

TABLE I (*contd.*)

Authors		Uchida, Ota, Wave-number	Int	Assignment	
Wave-length	Wave-number			System I v',v''	System II v',v''
5525.6	18093		1		11,6
5504.1	18163		1		9,5
5483.6	18231		1		12,6
5480.0	18243	18243.1	2	9,7	
5476.3	18255	18254.7	2	7,6	
5460.0	18310		1		10,5
5434.4	18396		2	12,8	
5428.6	18416	18415.8	2	10,7	
5425.9	18425i		2		
5424.2	18431		2	8,6	
5420.4	18444		2	6,5	
5417.4	18454		0		11,5
5388.3	18554		1		
5377.2	18592	17592.5	1		12,5
5373.3	18604	18604.3	1	9,6	
5368.1	18623		1	7,5	
5355.9	18666		1		10,4
5341.0	18718		0		
5335.6	18737		1		13,5
5330.6	18754		1	12,7	
5325.1	18774	18774.1	1	10,6	
5318.7	18796	18788.6	1	8,5	
5314.0	18813		1		11,4
5309.4	18829		1		
5304.2	18848		1		
5296.3	18876		2		14,5
5290.7	18896		2		
5285.2	18915	18914.4	4	13,7	
5277.3	18944	18944.5	4	11,6	
5273.3	18958		3		12,4

TABLE I (*contd.*)

Authors		Uchida, Ota	Int	Assignment	
Wave-length	Wave-number	Wave-number		System I v',v''	System II v',v''
5271.1	18966		3	9,5	
5266.3	18983	18981.9	2		
5264.9	18988		2	7,4	
5261.2	19001		1		
5256.3	19019		2		15,5
5249.5	19044		1		
5242.5	19070		1		
5234.1	19100		2		13,4
5280.8	19112	19112.5	3	12,6	
5224.6	19135		2	10,5	
5211.9	19181		2		11,3
5196.1	19240		2		14,4
5191.2	19258		2		
5186.6	19275		3	13,6	
5178.9	19304	19304.1	2	11,5	
5173.3	19325		3		12,3
5170.0	19337	19341.4	3	9,4	
5156.2	19386		1		15,4
5155.2	19392i		1		
5153.6	19398		2	16,7	
5142.8	19439	19440.7	4	14,6	
5138.7	19455		2		
5134.1	19472	19471.8	4	12,5	13,3
5126.2	19502		1	10,4	
5119.6	19527		1	8,3	
5113.4	19551		2		11,2
5105.3	19582		4		
5099.9	19603	19599.7	4	15,6	14,3
5096.0	19618		1		
5089.2	19644		2	13,5	

TABLE I (*contd.*)

Authors		Uchida, Ota Wave-number	Int	Assignment	
Wave-length	Wave-number			System I v', v''	System II v', v''
5081.2	19675		2	11,4	
5075.5	19697		3		12,2
5073.9	19703i		3	9,3	
5066.1	19733		2		
5061.9	19750		3		
5059.7	19758		5	16,6	15,3
5049.1	19800		4	14,5	
5038.9	19840		4	12,4	13,2
5032.5	19865		4	10,3	
5024.9	19895		4	8,2	
5020.4	19913		3	17,6	
5018.2	19922		4		11,1
5016.2	19930i		3		
5008.3	19961		5	15,5	
4996.5	20008		2	13,4	
4988.4	20041		2	11,3	
4972.8	20104		0		
4968.5	20121		2	16,5	
4966.4	20130		1		15,2
4963.8	20140i		1		
4957.7	20165		0	14,4	
4945.7	20214		6	12,3	13,1
4941.1	20233		3	10,2	
4933.4	20264i		4		
4930.8	20275		5	17,5	15,2
4928.3	20285i		4		
4923.5	20305		1		
4910.7	20358		2		14,1
4905.5	20380		3	13,3	
4898.2	20410		3	11,2	

TABLE I (*contd.*)

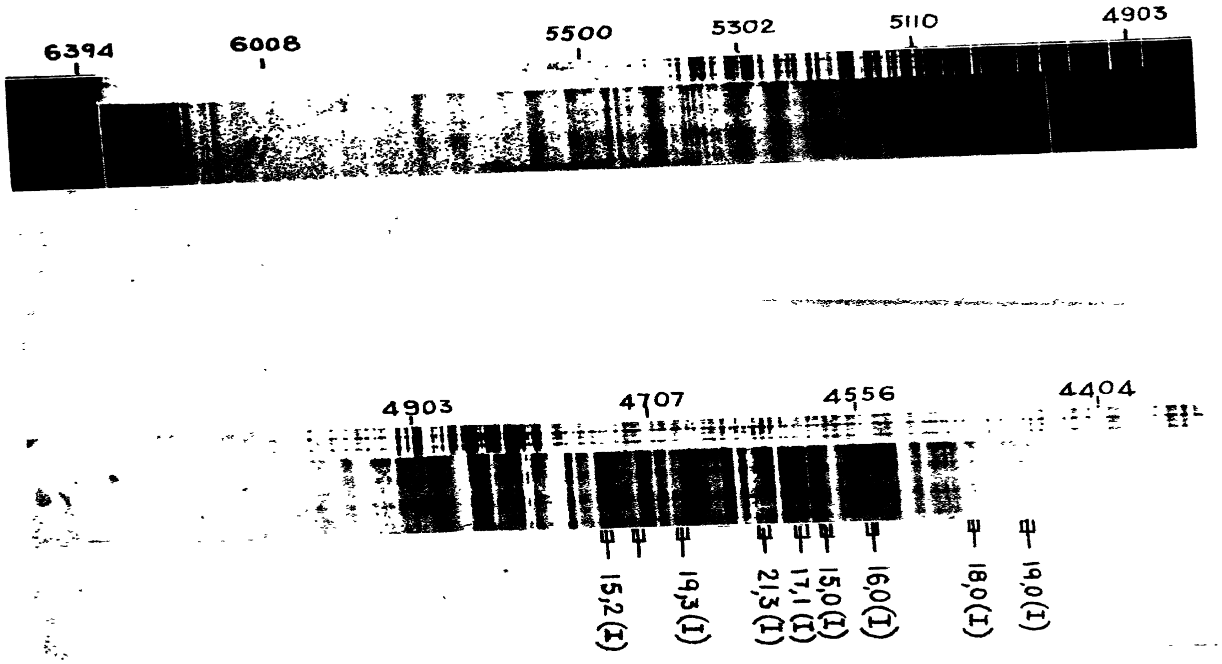
Authors		Uchida, Ota	Int	Assignment	
Wave-length	Wave-number	Wave-number		System I v', v''	System II v', v''
4891.0	20440		3		
4885.1	20465		3		
4878.5	20492		2	16,4	
4875.7	20504		3		15,1
4872.8	20516i		2		
4866.9	20541		4	14,3	
4858.0	20579		4	12,2	
4855.3	20590		8		13,0
4852.5	20603i		3		
4848.7	20618		3		
4845.0	20634i		1		
4842.3	20646		2	17,4	16,1
4839.3	20658i		1		
4830.5	20696i		2		
4828.8	20703		3	15,3	
4827.2	20710i		2		
4824.4	20722i		4		
4821.9	20733		4		14,0
4818.8	20746i		4	13,2	
4810.5	20782		1	11,1	
4797.0	20841		2		
4792.5	20860		3	16,3	
4790.3	20870i		2		
4788.0	20880		3		15,0
4782.6	20903		0	14,2	
4780.2	20914i		0		
4768.9	20963		1		
4766.7	20973i		0		
4756.0	21020		5	17,3	16,0
4747.8	21056i		2		

TABLE I (*contd.*)

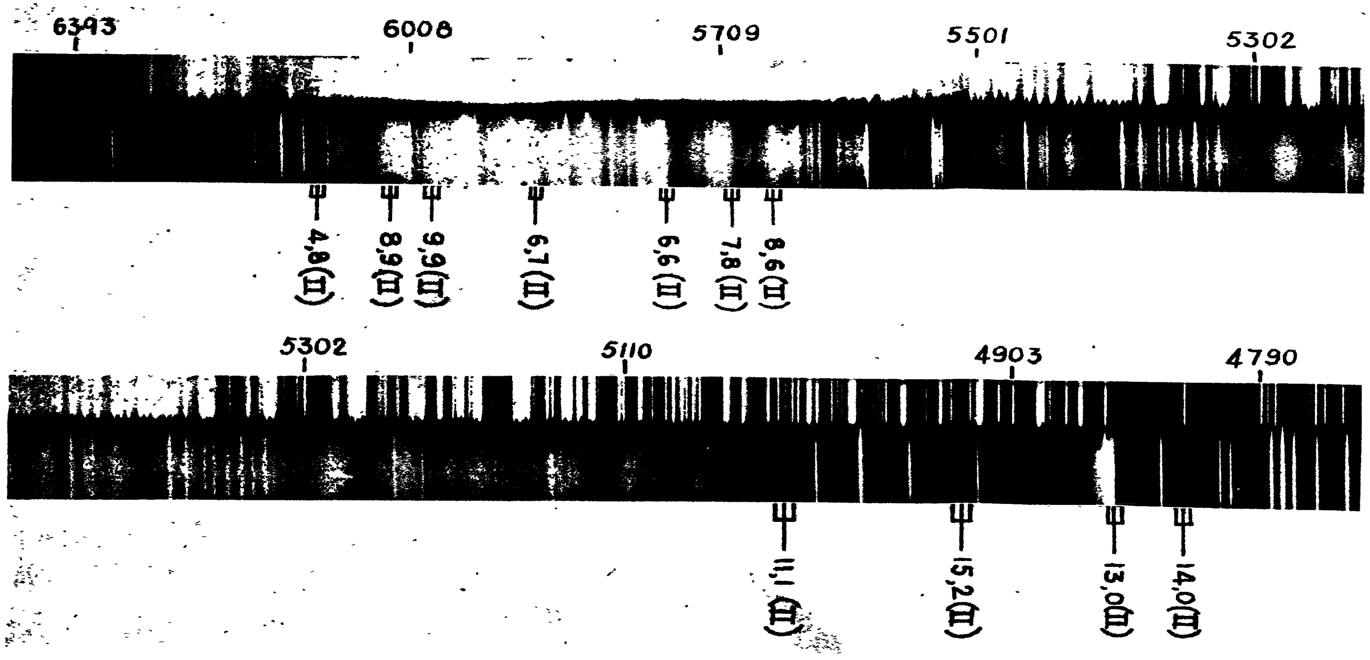
Authors		Uchida, Ota Wave-number	Int	Assignment	
Wave-length	Wave-number			System I v',v''	System II v',v''
4745.9	21065		3	15,2	
4743.2	21077i		2		
4734.8	21114		2	13,1	
4726.4	21152		3	11,0	
4722.2	21171		4	18,3	
4713.0	21212		0		
4708.8	21231		1	16,2	
4706.5	21241i		0		
4698.8	21276		1	14,1	
4695.7	21290i		0		
4691.3	21310i		2		
4689.1	21320		4	19,3	
4686.2	21333i		2		
4673.9	21389		2	17,2	
4670.6	21404i		1		
4664.6	21432i		2		
4662.3	21443		4	15,1	
4659.4	24156i		2		
4656.4	21470		4	20,3	
4653.9	21481i		3		
4652.4	21488		2	13,0	
4647.9	21509		2		
4640.5	21543		3	18,2	
4627.6	21603		3	16,1	
4625.1	21615		3	21,3	
4622.2	21629i		2		
4619.2	21643i		1		
4616.3	21656		1	14,0	
4608.9	21691		0	19,2	
4606.3	21703i		0		

TABLE I (*contd.*)

Authors		Uchida, Ota Wave-number	Int	Assignment	
Wave-length	Wave-number			System I v',v''	System II v',v''
4596.8	21748i		1		
4594.3	21760		2	17,1	
4590.4	21778i		1		
4587.1	21791		0		
4584.6	21806i		1		
4581.8	21819		2	15,0	
4578.5	21835i		1		
4567.1	21890i		2		
4563.6	21906		3	18,1	
4560.4	21992i		1		
4556.8	21939		1		
4553.1	21957i		1		
4549.7	21973		2	16,0	
4546.0	21991		2	21,2	
4542.5	22008i		1		
4536.9	22035		1		
4532.4	22057		1		
4520.6	22115i		2		
4517.2	22131		3	17,0	
4515.8	22138		3	22,2	
4507.3	22180		3		
4504.1	22196i		1		
4500.8	22212		4	20,1	
4492.7	22252		2		
4489.0	22270i		2		
4485.8	22286		3	18,0	
4482.1	22305 i		2		
4469.8	22366		0	21,1	
4463.1	22400		1		
4458.8	22421i		1		



Emission bands of bromine (Fuess spectrograms). Isotopes for some of the bands are bracketed. The longer limbs represent the component due to the abundant molecule.



Emission bands of bromine (Littrow spectrograms). Isotopes for some of the bands are bracketed. Longer limbs represent the component due to the abundant molecule.

TABLE I (*contd.*)

Authors		Uchida, Ota Wave-number	Int	Assignment	
Wave-length	Wave-number			System I v',v''	System II v',v''
4455.5	22438		2	19,0	
4451.9	22456i		1		
4449.1	22470		1		
4447.2	22480		1		
4444.7	22492		1		
4433.5	22549		1		
4430.6	22564i		1		
4427.3	22581		2	20,0	
4419.5	22621		1		
4416.7	22635		1		
4414.2	22648		1		
4394.8	22748		1		

Note : The wavenumbers marked with the letter "i" are the isotopic components of the neibhouring bands.

PLATES

The spectrum extending from λ 6700 to λ 4400 consists of more than 300 bands as against only 80 bands reported by UO in the region λ 6700 to λ 5000. Plate VA is a reproduction of the Fuess spectrogram and is shown in two strips. Among these some are red degraded, some are diffuse and others appear line-like. There is a gradual fall in the intensity of the spectrum towards the shorter wavelengths. Bands on the less refrangible side appear unresolved, probably due to the lower dispersion. Below λ 5300 the bands appear sharp and well resolved. Below λ 4400 there appears a continuum overlaid by perhaps, two or three groups of discrete bands.

Plate VB is the reproduction of the spectrum in the region λ 6400 to λ 4800 recorded on the glass Littrow instrument and is shown in two strips.

TABLE II

System I

Vibrational scheme due to Uchida and Ota

v' \ v''	0	1	2	3	4	5	6
0					15893.6		15195.7
1				16434.4	16080.4	15725.1	15381.7
2				16625.7	16269.4	15914.1	15569.1
3				16814.2	16457.4	16107.3	
4				16993.1	16649.2	16287.7	
5				17178.2	16828.3	16474.8	16123.0
6		18080.7	17718.6	17361.4	17000.3		16300.4
7		18254.7	17896.6	17539.3			
8			18070.3	17710.8			
9		18604.3	18243.1				
10		18774.4	18415.8				
11	19304.1	18944.5	18584.2				
12	19471.8	19112.5	18749.1				
13			18914.4				
14		19440.7					
15		19599.7					

TABLE III

System II

Vibrational scheme due to Uchida and Ota

v' \ v''	0	1	2	3	4
0			15381.7		
1			15533.5		
2			15689.0	15333.9	
3			15841.9	15478.3	15137.9
4			15991.7	15638.2	15284.6
5			16139.1	15786.4	15435.9
6		16640.9	16287.7	15935.1	15587.3
7		16789.4	16434.4	16080.4	
8		16930.1	16585.2		
9	17442.3	17083.1	16729.5		
10	17586.2	17233.2			

ANALYSIS

As has already been mentioned the bands obtained by UO in the region λ6700 to λ 5000 were analysed into two systems which are shown in Tables II and III. With the prominent band heads among the 80 bands they formed a small number of genuine progressions. The vibrational formulae derived from the analyses are given in the introduction. The lower state is common for both the systems. The intensity distribution in the two systems is of an open Franck-Condon parabola type which is in keeping with such divergent values of ω'_e and ω''_e. However, the vibrational assignments were not supported by the study of bromine isotope effect and are quite arbitrary.

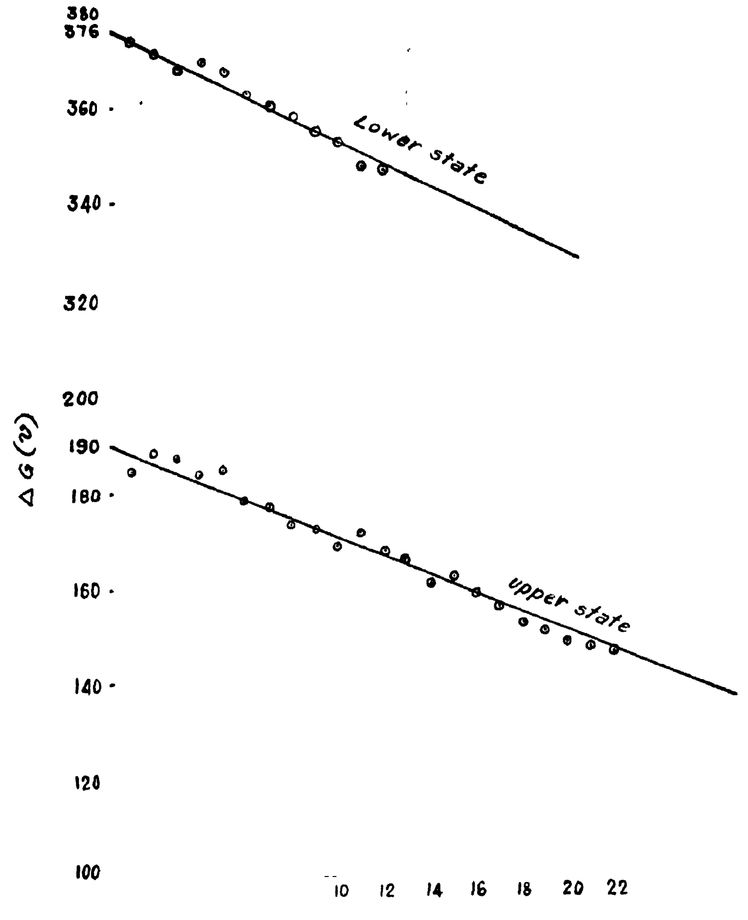


Fig. 1 System I

With the present data of more than 300 bands in the extensive region λ 6700 to λ 4400 it is found possible to extend the above two analyses considerably.

Not only some of the previous progressions are considerably extended, but, many more new progressions could be developed in both the systems. The newly formed vibrational schemes are shown in Tables IV and V. This extension has necessitated a renumbering of the bands and also a redetermination of the vibrational constants. The constants are extapolated by drawing the usual $\Delta G(v)-v$ curves which are found to be linear. These curves are shown in figures 1 and 2.

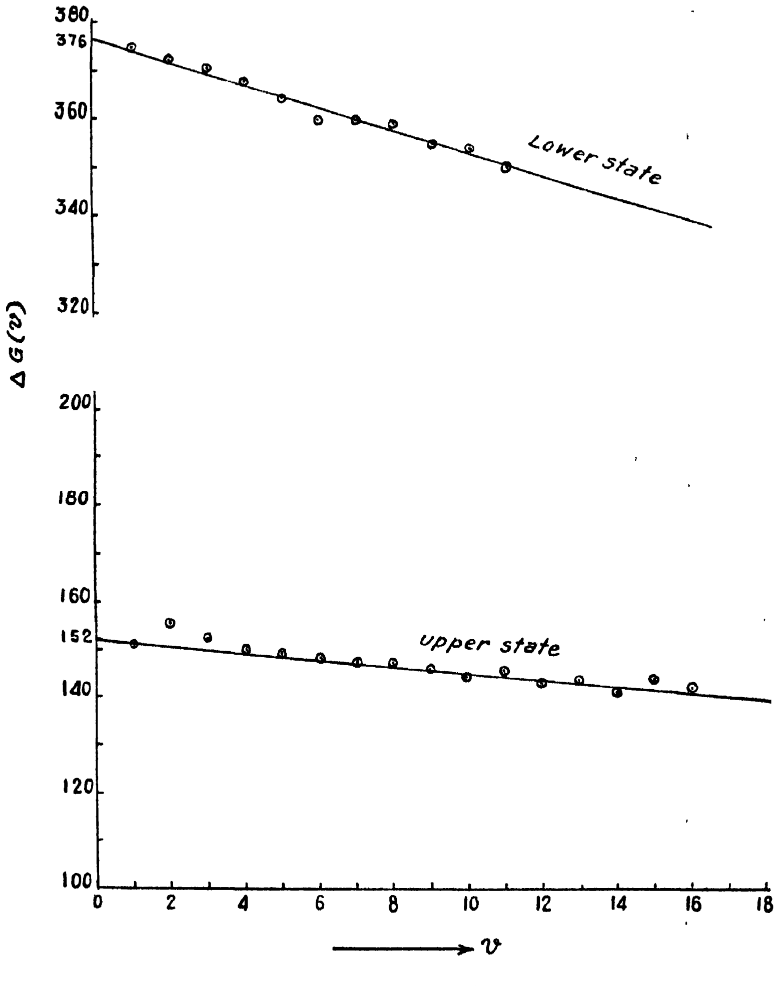


Fig. 2. System II

The following vibrational formulae represent the two systems.

System I $\nu = 19290+190.0(v'+\frac{1}{2})-1.0(v'+\frac{1}{2})^2 -376.0(v''+\frac{1}{2})+1.25(v''+\frac{1}{2})^2$

System II $\nu = 18782+152.0(v'+\frac{1}{2})-0.35(v'+\frac{1}{2})^2 -376.0(v''+\frac{1}{2})+1.25(v''+\frac{1}{2})^2$

TABLE IV

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12
0									16250	15894		15196	
1									16434	16080	15725	15382	
2								16986	16626	16269	15914	15569	
3								17174	16814	16457	16107	15760	
4								17361	17003	16649	16288	15935	15587
5							17906	17540	17182	16828	16475	16123	15773
6						18444	18081	17719	17361*			16300	15949
7					18988	18623	18255	17897	17540*				
8			19895	19527		18796	18431	18070	17710				
9			×	19703	19337	18966	18604	18243	17886				
10			20233	19865	19502	19135	18774	18416					
11	21152	20782	20410	20041	19675	19304	18944						
12	21320		20579	20214	19840	19472	19112	18754					
13	21488	21114	20746	20380	20008	19644	19275	18915					
14	21656	21276	20903	20541	20165	19800	19439						
15	21819	21443	21065	20703	×	19961	19603						
16	21973	21603	21231	20860	20492	20121	19758						
17	22131	21760	21389	21020	20646	20275	19913						
18	22286	21906	21543	21171	×								
19	22438	×	21691	21320*									
20	22581	22212		21470									
21			21991	21617									
22			22138	×	21404								

Note : The bands marked with (*) occur twice. The places marked × are superposed by atomic lines.

TABLE V

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11
0										15382		
1										15533		
2										15689	15334	
3										15842	15487	15138
4									16347	15992	15638	15285
5									16497	16139	15786	15436
6							17361	17003	16641	16288	15935	15587
7						17871	17512	17147	16789	16434	16080	
8						18019	17663	×	16930	16585		
9					×	18163	17804	17442	17083	16729		
10					18666	18310	17944	17586	17223			
11		19922	19551	19181	18813	18454	18093					
12		×	19697	19325	18958	18592	18231					
13	20590	20214	19840	19472	19100	18737						
14	20733	20358	×	19603	19240	18876						
15	20880	20504	20130	19758	19386	19019						
16		20646	×									

Note : The places marked × are superposed by atomic lines.

The lower state 376.0 is again common for both the systems. The intensity distribution in both the systems is still of open Franck-Condon parabola type and is consistent with the order of ω'_e and ω''_e values obtained above. An examination of the vibrational arrays shown in Tables IV and V reveals that there are bands common to both the systems. This is a feature which can also be seen from the vibrational arrays of UO shown in Tables II and III.

ISOTOPE EFFECT

Further confirmation of these analysis could be obtained from a study of the bromine isotope effect. It is well known that bromine has got two isotopes of mass numbers 79 and 81, out of which three components due to the three molecules are to be observed in its molecular spectrum. The three molecules are ($Br^{79}Br^{79}$), ($Br^{79}Br^{81}$), ($Br^{81}Br^{81}$). The relative abundance ratio of these molecules is as 1:2:1 respectively. In the band spectrum of Br_2, for bands on the violet side of the system origins, i.e. with $\nu > \nu_e$ the separation of the isotopic component ($Br^{79}Br^{79}$) with respect to the component of the more abundant molecule ($Br^{79}Br^{81}$) is positive and the corresponding separation for the component of ($Br^{81}Br^{81}$) is negative. For the bands on the red side of the system origins, i.e., with $\nu < \nu_e$ the opposite is the case. The isotope separations with respect to the more abundant molecule, $\Delta\nu$, are calculated according to the formula

$$\nu^i - \nu = (\rho - 1)[\omega'_e(v' + \tfrac{1}{2}) - \omega''_e(v'' + \tfrac{1}{2})] - (\rho^2 - 1)[x'_e\omega'_e(v' + \tfrac{1}{2})^2 - x''_e\omega''_e(v'' + \tfrac{1}{2})^2].$$

An examination of the vibrational schemes shown in Tables IV and V, reveals bands with large differences in the values of v' and v''. For such bands the isotope separations for the less abundant molecules calculated from the above formula are found to be large and may be expected to be resolved even under the low dispersion of the Fuess instrument. For example, the calculated separations of the two components for 15,0 band in system I are 16.2 and 13.8. The isotopic componnents for some of these bands are expected to coincide with the position of the main bands assigned to the same system. In Table I, some of the main bands occur as isotopic heads of the neighbouring bands belonging to the same system.

For a large number of the bands the agreement between the observed and calculated separations as can be seen from Table VI is quite satisfactory. On Plates VA and VB the isotopic components are bracketted for some of the bands.

TABLE VI

Isotope effect

SYSTEM I.						SYSTEM II.					
(Br^{79}Br^{81})		(Br^{79}Br)^{79}		(Br^{81}Br^{81})		(Br^{79}Br^{81})		(Br^{79}Br^{79})		(Br^{81}Br^{81})	
v'	v''	Cal.	Obs.	Cal.	Obs.	v'	v''	Cal.	Obs.	Cal.	Obs.
15,	0	16.2	16	13.8	13	13,	0	13.0	13	11.3	11
16,	0	17.0	18	14.8	16	14,	0	14.0	13	12.2	11
17,	0	18.0	*	15.8	16	11,	1	8.2	8	7.1	9
18,	0	18.7	19	16.8	16	15,	1	12.4	12	10.8	12
19,	0	19.6	18	16.8	17	16,	1	13.4	12	11.7	12
20,	0	20.3	*	17.8	17	15,	2	9.9	10	8.6	9
15,	1	13.5	13	11.5	11	16,	2	10.9	11	9.5	11
16,	1	14.3	14	12.5	*	6,	6	9.7	13	8.4	11
17,	1	15.3	18	13.5	12	7,	6	8.6	8	7.4	*
18,	1	16.0	16	14.5	16	8,	6	7.5	9	6.5	7
20,	1	17.6	*	15.5	16	6,	7	12.1	15	10.6	11
14,	2	10.1	13	8.8	*	7,	7	11.0	*	9.6	11
15,	2	11.0	12	9.3	9	9,	7	8.9	9	7.8	9
19,	2	14.4	12	12.3	*	4,	8	16.4	17	14.5	15
21,	2	15.9	17	13.3	13	6,	8	14.4	15	12.7	*
15,	3	8.4	7	7.0	7	7,	8	13.3	13	11.7	13
19,	3	11.8	13	10.0	10	8,	8	13.3	13	10.8	11
20,	3	12.5	11	11.0	14	9,	8	11.2	10	9.9	10
21,	3	13.3	14	11.5	12	10,	8	10.2	10	8.8	10
2,	7	15.7	16	13.8	17	4,	9	18.9	20	16.5	17
4,	7	13.2	13	11.6	11	5,	9	17.9	17	15.5	17
5,	7	12.0	12	10.5	8	6,	9	16.9	19	14.7	*
6,	7	10.8	9	9.4	7	8,	9	14.7	15	12.8	17
7,	7	10.0	11	8.5	9	9,	9	13.7	13	11.9	10
8,	7	8.6	*	7.5	11	6,	10	19.1	21	16.8	14

TABLE VI (*Contd.*)

SYSTEM I						SYSTEM II
($Br^{79}Br^{81}$) v' v''		($Br^{79}Br^{79}$) Cal.	Obs.	($Br^{81}Br^{81}$) Cal.	Obs.	
2,	8	18.0	*	15.9	15	
3,	8	16.8	*	14.7	14	
4,	8	15.5	17	13.7	[illegible]	
6,	8	13.1	13	11.5	11	
7,	8	12.3	12	10.6	8	
0,	9	23.0	24	20.1	20	
1,	9	21.8	22	18.9	*	
2,	9	20.5	19	17.9	19	
3,	9	19.3	23	16.7	18	
4,	9	18.0	23	15.7	16	
5,	9	16.8	14	14.6	15	
1,	10	24.0	22	21.0	*	
2,	10	22.7	20	20.0	21	
3,	10	21.5	27	18.8	16	
5,	10	19.0	18	16.7	22	
5,	11	21.4	16	18.7	16	
6,	11	20.2	20	17.6	17	

Note : The places marked (*) are superposed by atomic lines.

CONCLUSIONS

In the foregoing pages, the vibrational analyses of the emission bands of bromine, as belonging to two different systems, are reported. As has already been pointed out, these emission bands do not bear any relationship with the absorption bands due to the neutral bromine molecule. Further, the vibrational frequency 376 cm^{-1} which is common to both the above systems does not correspond to any one of the vibrational frequencies known till now to the neutral molecule. It is also interesting to note that this frequency comes nearer to the value 361 cm^{-1} predicted by Mulliken (1934) as the most probable value of the ground state of the ionised molecule Br_2^+. The above considerations will lead one to conjecture that the emitter of the above two systems may be the ionised molecule Br_2^+. However, confirmation of this view can only be obtained by a study of the rotational analysis of some of these bands which will also lead to a clear understanding of the nature of the levels involved. Work in this direction is in progress.

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REFERENCES

Elliot, A., and Cameron, W. H. B., 1937, *Proc. Roy. Soc. A.*, **158**, 681.
„ 1938, *Ibid* **164**, 531.
Howell, H. G., 1953, *Proc. Phys. Soc. A.*, **66**, 759.
Mulliken, R. S., 1934, *Phys. Rev.*, **46**, 549.
Uchida, Y., and Ota, Y., 1928, *Jap. J. Phys.*, **5**, 53.
„ *Ibid* **5**, 59.