THE EMISSION SPECTRUM OF BISMUTH BROMIDE (BiBr)—"A" SYSTEM

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INTRODUCTION

As part of their extensive study of the emission spectra of the halides of the elements of groups IV and V of the periodic table, Howell and Rochester (1934) obtained the molecular spectrum of BiBr using high frequency discharge. Morgan (1936), in his detailed investigation of the absorption spectra of Bismuth halides, obtained two systems in absorption, one in the region $\lambda\lambda$ 4595–5438, and the other in the region $\lambda\lambda$ 3862–4129, both attributable to the molecule BiBr. On the other hand Sur and Majumdar (1954) obtained three systems in absorption for BiBr in the regions $\lambda\lambda$ 2709–2968, $\lambda\lambda$ 2336–2450 and $\lambda\lambda$ 2200–2350. They designated these systems as C, D and E respectively, naming the other two long wavelength systems as A and B. No detailed vibrational analysis of the A-system has been made in emission.

Our knowledge of the band spectra of the other bismuth halides is far more extensive [Howell (1936), Saper (1931), Rochester (1937), P. T. Rao (1949), Sur (1950), Ray (1942), P. Venkateswarlu and B. N. Khanna (1960), B. N. Khanna (1961), K. C. Joshi (1961), G. D. Rochester (1961), Prasada Rao and Rao, P. T. (1962)]. Consequently, a study of the A-system of BiBr in emission was undertaken. In this, a transformer discharge may be expected to yield a more complete spectrum and enable us improve our knowledge of the vibrational constants of the states involved and also the isotope effect in the band spectrum of bismuth monobromide.

EXPERIMENTAL

Extra pure anhydrous bismuth tribromide was taken in a small cavity at the centre of a conventional type of discharge tube (fused silica) 30 cm. long and of about 1·1 cm. in diameter. Hollow nickel electrodes were fitted coaxially inside the silica tube with their nearer ends separated by a

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distance of about 6 cm. and placed symmetrically on either side of the cavity containing the salt. Pyrex adopters through which aluminium rods of diameter 2 mm. could be introduced were fitted to the ends of the discharge tube. The nickel electrodes were connected to these aluminium rods by means of a short piece of nichrome wire. To one end of the discharge tube was attached a glass window through which the discharge could be observed end on. The other end was provided with a side tube through which the tube can be evacuated. Standard precautions were taken to avoid contamination of the discharge and also to protect the pumping system from vapours. Uncondensed transformer discharge (15,000 V, 30 mA) was used for excitation and the voltage applied to the discharge tube could be varied by altering the input voltage of the transformer by means of a variac. The substance was vapourised by a careful and controlled heating of the substance and the discharge was deep green in colour. Fuess and El glass Littrow spectrographs were employed to photograph the spectra. An exposure of about half an hour was found to be adequate to record the spectrum with Ilford special rapid panchromatic plate in the case of the lower dispersion instrument while an exposure of one hour was found necessary with the Littrow spectrograph and Ilford rapid process panchromatic plates. The band heads were measured against iron arc standards and the wave number values of the band heads reported here are accurate to ± 2 cm.$^{-1}$ in general while on the long wavelength side it may be a little less on account of lower dispersion.

RESULTS

The band spectrum of BiBr obtained has been reproduced in Plate V. Figure 1 represents the spectrogram obtained with Fuess while Fig. 2 shows that recorded with the Littrow instrument. The wavelengths of the bands, the corresponding wave numbers in vacuum, their visually estimated relative intensities and the assignment of the vibrational quantum numbers have been given in Table I. The A-system is found to extend from λ 4595–6063, while some bands could be observed even slightly beyond 6063 Å. All the bands are red-degraded and are of the progression type. This system has been previously observed only up to 5438 Å. In all, about 286 bands were recorded in emission in the present study while Morgan reported only 61 in absorption. The B-system of BiBr observed by Morgan was also obtained now in emission in the same region (see Fig. 1, Plate V). In this system, the first three members of the (0, 0) sequence are red-degraded while the sequence itself is violet-degraded. The other bands are line-like. This system is not as fully developed as in absorption. It is worth pointing out that this B-system bears some resemblance to the corresponding system of BiI obtained by Rao (loc. cit.)

and an analogous system was not observed by Venkateswarlu and Khanna in BiCl.

TABLE I

BiBr bands

λ in Å	Int.	Observed ν in cm.$^{-1}$	Assignment v', v''	Calcu- lated ν	Morgan's value
6062·2	2	16491	4, 23 (81)	16492	
6051·9	2	16519	3, 22 (79)	16519	
6045·2	2	16537	12, 27 (79)	16537	
6041·8	1	16546	8, 25 (79)	16546	
6031·2	3	16575	12, 27 (81)	16575	
			2, 21 (79)	16577	
6029·0	2	16581	5, 23 (79)	16580	
6021·6	3	16602	17, 28 (79)	16603	
6020·2	3	16606	13, 27 (79)	16607	
6016·8	2	16615	16, 28 (81)	16616	
6009·2	3	16636	1, 20 (79)	16635	
6006·2	4	16644	13, 27 (81)	16645	
			4, 22 (79)	16645	
			11, 26 (79)	16643	
6001·1	1	16661	7, 24 (81)	16659	
5998·8	3	16665	14, 27 (79)	16668	
5987·9	3	16695	6, 23 (79)	16698	
5980·8	3	16715	15, 27 (79)	16718	
5978·7	2	16721	12, 26 (79)	16722	
5974·8	3	16732	8, 24 (79)	16732	
5971·5	3	16741	10, 25 (79)	16742	
			3, 21 (81)	16741	
5970·1	3	16745	7, 23 (81)	16745	
5966·6	3	16755	15, 27 (81)	16758	
5964·3	1	16761	12, 26 (81)	16758	
5953·2	3	16793	13, 26 (79)	16792	
5949·6	3	16803	18, 27 (79)	16803	
5940·1	3	16830	13, 26 (81)	16828	
			11, 25 (79)	16828	
5937·8	2	16836	4, 21 (79)	16835	
5930·6	3	16857	1, 19 (81)	16858	
5915·7	2	16899	3, 20 (79)	16898	
5908·4	2	16920	8, 23 (79)	16919	
5873·6	2	17020	1, 18 (79)	17018	
5871·1	3	17027	4, 20 (79)	17025	
5867·0	2	17039	14, 25 (79)	17037	
5863·2	3	17050	1, 18 (81)	17048	
			10, 23 (81)	17047	
5843·7	2	17107	8, 22 (79)	17107	
			0, 17 (81)	17106	

Table I (Contd.)

λ in A	Int.	Observed ν in cm.$^{-1}$	Assignment v', v''	Calculated ν	Morgan's value
5840·6	3	17116	10, 23 (79)	17115	
5821·9	3	17171	18, 25 (79)	17172	
			14, 25 (81)	17173	
5816·3	3	17185	7, 21 (79)	17189	
5811·9	3	17201	11, 23 (79)	17202	
5810·2	3	17206	9, 22 (79)	17208	
5808·3	3	17211	1, 17 (79)	17210	
5798·7	3	17240	9, 22 (81)	17239	
			1, 17 (81)	17240	
5793·7	2	17255	14, 24 (81)	17257	
5790·9	2	17263	16, 25 (81)	17265	
5786·3	2	17277	3, 18 (79)	17280	
5777·0	2	17305	10, 22 (79)	17303	
5767·8	2	17332	10, 22 (81)	17333	
5764·7	3	17342	2, 17 (79)	17343	
5759·3	3	17358	18, 24 (79)	17358	
5756·9	3	17365	5, 19 (81)	17366	
5748·4	1	17391	11, 22 (79)	17390	
5745·7	2	17399	9, 21 (79)	17398	
5739·7	1	17417	11, 22 (81)	17419	
5736·9	3	17426	9, 21 (81)	17426	
5725·6	1	17460	6, 19 (79)	17458	
5723·0	3	17468	12, 22 (89)	17468	
			17, 23 (81)	17466	
5716·1	2	17489	19, 23 (81)	17490	
5713·6	2	17497	12, 22 (81)	17498	
5711·4	3	17503	16, 23 (79)	17501	
5703·6	3	17527	17, 23 (79)	17529	
5701·4	3	17534	2, 16 (79)	17536	
5696·6	2	17549	19, 23 (79)	17550	
5693·7	3	17558	5, 18 (81)	17556	
5690·2	1	17569	7, 19 (79)	17571	
5681·4	3	17596	7, 19 (81)	17596	
			1, 15 (79)	17599	
5673·1	2	17622	1, 15 (81)	17624	
5662·1	3	17656	12, 21 (79)	17657	
5659·8	3	17663	0, 14 (79)	17660	
5651·7	3	17688	12, 21 (81)	17686	
			16, 22 (79)	17689	
5646·5	1	17705	8, 19 (81)	17703	
5642·9	1	17716	17, 22 (79)	17717	
5638·9	3	17729	2, 15 (79)	17731	
5633·8	3	17745	5, 17 (81)	17747	
5631·4	2	17752	17, 22 (81)	17752	

TABLE I (*Contd.*)

λ in A	Int.	Observed ν in cm. [1]	Assignment v', v''	Calculated ν	Morgan's value
5627·7	2	17764	7, 18 (79)	17762	
5624·6	1	17774	19, 22 (81)	17777	
5621·9	2	17782	9, 19 (79)	17780	
5618·6	2	17793	4, 16 (79)	17794	
5614·4	1	17806	9, 19 (81)	17804	
5611·1	2	17816	4, 16 (81)	17817	
5604·8	1	17836	15, 21 (79)	17838	
5602·0	0	17845	12, 20 (79)	17847	
5593·8	1	17871	15, 21 (81)	17869	
5585·1	2	17899	10, 19 (81)	17898	
5581·4	1	17911	16, 21 (81)	17910	
5577·1	3	17925	2, 14 (79)	17927	
5570·0	3	17948	2, 14 (81)	17949	
5563·0	0	17970	9, 18 (79)	17970	
5560·1	3	17980	14, 20 (79)	17977	
5557·1	2	17990	1, 13 (79)	17991	
5549·7	2	18014	1, 13 (81)	18013	
5545·2	2	18028	15, 20 (79)	18028	
5538·0	1	18052	0, 12 (79)	18054	
5535·1	1	18061	8, 17 (79)	18062	
5530·9	1	18075	0, 12 (81)	18075	
5528·4	1	18083	8, 17 (81)	18084	
5516·6	3	18122	2, 13 (79)	18124	
5510·1	3	18143	2, 13 (81)	18144	
5503·6	0	18164	9, 17 (79)	18163	
5499·0	3	18180	4, 14 (79)	18183	
5496·6	2	18188	1, 12 (79)	18188	
5492·6	3	18201	4, 14 (81)	18204	
5490·5	2	18208	1, 12 (81)	18208	
5484·2	1	18229	6, 15 (79)	18229	
5479·4	3	18245	15, 19 (81)	18246	
5477·4	3	18251	6, 15 (81)	18250	
			0, 11 (79)	18252	
5471·2	3	18272	0, 11 (81)	18272	
5462·7	2	18300	13, 18 (79)	18300	
5457·0	3	18320	2, 12 (79)	18321	
5451·6	3	18338	2, 12 (81)	18340	
5440·2	2	18376	9, 16 (81)	18377	
5437·3	3	18386	1, 11 (79)	18387	18385·6
5431·5	3	18406	1, 11 (81)	18406	18404·6
5429·4	2	18413	15, 18 (79)	18411	
5427·3	2	18420	12, 17 (79)	18423	
5419·9	3	18445	12, 17 (81)	18445	
5418·2	4	18451	0, 10 (79)	18451	18450·8

Table I (*Contd.*)

λ in A	Int.	Observed ν in cm. [1]	Assignment v', v''	Calculated ν	Morgan's value
5412·8	5	18469	0, 10 (81)	18469	·18469·2
5405·6	2	18494	13, 17 (79)	18493	
5403·9	3	18500	19, 18 (79)	18499	
5400·2	3	18512	13, 17 (81)	18515	
5397·1	5	18523	5, 3 (81)	18521	
5393·1	3	18537	11, 16 (79)	18538	
5387·6	3	18555	14, 17 (79)	18553	
5381·7	3	18576	14, 17 (81)	18576	
			4, 12 (79)	18577	
5378·9	4	18586	1, 10 (79)	18586	18585·0
5376·5	3	18594	4, 12 (81)	18595	
5373·4	4	18605	1, 10 (81)	18603	18603·4
5370·9	3	18614	12, 16 (79)	18616	
5369·3	3	18619	6, 13 (79)	18621	
5363·4	4	18639	6, 13 (81)	18639	
5360·1	6	18651	0, 9 (79)	18652	18652·2
5355·3	6	18667	0, 9 (81)	18668	18668·1
5350·4	2	18685	13, 16 (79)	18686	
5348·4	2	18691	19, 17 (79)	18692	
5347·0	3	18696	17, 17 (81)	18699	
5343·7	2	18708	13, 16 (81)	18707	
5340·7	2	18718	2, 10 (79)	18718	
5339·4	2	18723	19, 17 (81)	18723	
5337·5	1	18730	11, 15 (79)	18732	
5336·1	1	18735	2, 10 (81)	18734	
5327·6	2	18764	9, 14 (81)	18764	
5326·2	1	18769	14, 16 (81)	18769	
5321·5	1	18786	1, 9 (79)	18786	18786·8
5317·1	1	18802	1, 9 (81)	18802	18802·2
5305·8	3	18842	8, 13 (79)	18842	
5303·0	6	18852	0, 8 (79)	18853	18852·6
5300·7	3	18860	8, 13 (81)	18858	
5298·5	6	18868	0, 8 (81)	18868	18867·5
5294·4	2	18882	13, 15 (79)	18881	
			18, 16 (79)	18882	
5291·5	3	18892	17, 16 (81)	18891	
5285·1	4	18915	19, 16 (81)	18915	
			5, 11 (81)	18913	
5281·2	3	18929	11, 14 (79)	18928	
5280·2	1	18933	2, 9 (81)	18933	
5275·6	3	18949	7, 12 (81)	18947	
5267·7	5	18978	4, 10 (79)	18975	
5265·7	5	18985	1, 8 (79)	18987	
5263·2	2	18991	15, 15 (79)	18991	

TABLE I (*Contd.*)

λ in A	Int.	Observed ν in cm. [1]	Assignment v', v''	Calculated ν	Morgan's value
5261·3	3	19001	1, 8 (81)	19001	
5257·2	3	19016	6, 11 (79)	19017	
5255·0	3	19024	12, 14 (81)	19024	
5253·4	4	19030	6, 11 (81)	19031	
			16, 15 (79)	19031	
5246·7	10	19054	0, 7 (79)	19055	19054·6
5242·8	10	19068	0, 7 (81)	19068	19067·9
5240·3	1	19077	13, 14 (79)	19076	
5235·8	1	19093	13, 14 (81)	19094	
5232·8	5	19104	18, 15 (81)	19102	
5230·9	2	19111	5, 10 (81)	19111	
5229·2	8	19118	2, 8 (79)	19120	
5226·9	3	19126	11, 13 (79)	19124	
5225·2	9	19132	2, 8 (81)	19132	
5213·7	7	19174	4, 9 (79)	19175	
5205·3	3	19205	12, 13 (79)	19203	
5204·4	3	19209	15, 14 (81)	19207	
5201·7	3	19215	6, 10 (79)	19216	
5198·6	4	19230	6, 10 (81)	19228	
5197·1	4	19236	10, 12 (79)	19235	
5191·1	9	19258	0, 6 (79)	19258	19257·6
5188·1	9	19269	0, 6 (81)	19269	19268·6
5187·2	1	19272	18, 14 (79)	19272	
5185·6	1	19278	19, 14 (79)	19276	
5179·7	2	19300	5, 9 (79)	19298	
			19, 14 (81)	19302	
5177·6	1	19308	5, 9 (81)	19309	
5174·1	1	19321	2, 7 (79)	19322	19320·9
5170·9	1	19333	2, 7 (81)	19333	19330·5
5166·9	1	19348	14, 13 (81)	19350	
5159·6	1	19375	4, 8 (79)	19376	
5158·0	1	19381	15, 13 (79)	19383	
5157·1	1	19385	4, 8 (81)	19387	
5154·7	1	19394	1, 6 (79)	19392	
5153·1	1	19400	1, 6 (81)	19402	
5149·1	3	19415	6, 9 (79)	19416	
5147·0	3	19423	16, 13 (79)	19423	
5142·0	3	19442	16, 13 (81)	19442	
5138·7	3	19454	3, 7 (79)	19452	
5137·0	8	19461	3, 7 (81) ,	19461	
			0, 5 (79)	19462	19461·4
5134·0	5	19472	0, 5 (81)	19471	19470·5
5130·3	5	19486	13, 12 (81)	19485	
5127·0	5	19499	5, 8 (79)	19499	

Table I (Contd.)

λ in A	Int.	Observed ν in cm.$^{-1}$	Assignment v', v''	Calculated ν	Morgan's value
5125·2	4	19506	5, 8 (81)	19509	
5121·8	4	19518	11, 11 (79)	19520	
5119·7	5	19526	2, 6 (79)	19525	
5117·6	8	19534	2, 6 (81)	19534	
			11, 11 (81)	19532	
5114·5	5	19546	14, 12 (81)	19545	
5101·7	6	19595	1, 5 (79)	19596	19596·3
5099·4	6	19604	1, 5 (81)	19605	19604·6
5096·0	2	19617	6, 8 (79)	19618	
5093·7	2	19626	6, 8 (81)	19626	
5091·1	10	19636	16, 12 (81)	19638	
			10, 10 (79)	19633	
			8, 9 (79)	19637	
5088·2	4	19647	8, 9 (81)	19647	
5086·5	8	19654	3, 6 (79)	19655	
5084·3	8	19662	3, 6 (81)	19663	
5083·2	4	19667	0, 4 (79)	19666	19666·8
5081·3	4	19674	0, 4 (81)	19674	19674·5
5078·6	2	19684	13, 11 (81)	19681	
5075·2	5	19698	5, 7 (79)	19701	
5069·8	2	19719	11, 10 (79)	19719	
5067·4	5	19728	11, 10 (81)	19730	
			2, 5 (79)	19729	
5065·6	3	19735	2, 5 (81)	19736	
5063·2	2	19744	14, 11 (81)	19742	
5048·5	5	19802	1, 4 (79)	19801	19801·3
5046·8	5	19809	1, 4 (81)	19808	19807·8
5044·8	2	19816	6, 7 (79)	19819	
5040·7	2	19833	10, 9 (79)	19833	
5037·9	3	19844	10, 9 (81)	19842	
5033·9	2	19859	3, 5 (79)	19859	
5032·0	1	19867	3, 5 (81)	19865	
5029·4	3	19877	0, 3 (81)	19878	
5018·6	2	19920	11,9 (79)	19920	
5016·0	6	19930	2, 4 (79)	19933	19932·7
5014·4	7	19937	2, 4 (81)	19939	19937·6
5012·3	5	19945	9, 8 (81)	19947	
5005·0	6	19974	15, 10 (79)	19978	
5002·2	7	19985	4, 5 (79)	19985	
4999·2	3	19998	12, 9 (79)	19998	
4996·9	7	20006	12, 9 (81)	20007	
			1, 3 (79)	20006	20007·6
4996·1	4	20010	1, 3 (81)	20012	20012·6
4994·8	3	20015	16, 9 (79)	20018	

TABLE I (*Contd.*)

λ in A	Int.	Observed ν in cm.[1]	Assignment v′, v″	Calculated ν	Morgan's value
4991·1	1	20030	6, 6 (81)	20028	
4988·6	2	20040	8, 7 (79)	20040	
4987·1	2	20046	17, 10 (79)	20047	
4983·5	2	20060	17, 10 (81)	20062	
4981·9	2	20067	19, 10 (79)	20067	
			13, 9 (79)	20068	
4977·7	3	20084	0, 2 (81)	20083	20079·1
4972·2	2	20106	·5, 5 (79)	20108	
4970·5	2	20113	5, 5 (81)	20112	
4968·2	3	20122	11, 8 (79)	20121	
4966·6	4	20128	11, 8 (81)	20128	
4965·1	5	20134	7, 6 (79)	20136	
4964·0	5	20139	2, 3 (79)	20139	20140·0
4962·9	5	20143	2, 3 (81)	20143	20143·4
4954·0	3	20180	15, 9 (79)	20179	
4951·8	3	20189	15, 9 (81)	20190	
4950·0	3	20196	12, 8 (79)	20199	
4946·6	4	20214	1, 2 (79)	20213	
4940·9	5	20233	10, 7 (79)	20236	
4939·3	5	20240	10, 7 (81)	20241	
4938·5	5	20243	8, 6 (79)	20243	
4933·2	7	20265	18, 9 (79)	20263	
4931·8	6	20270	3, 3 (79)	20269	20268·8
4922·0	4	20311	5, 4, (79)	20313	
4918·9	4	20324	11, 7 (79)	20323	
4917·9	4	20328	11, 7 (81)	20328	
4916·0	6	· 20336	7, 5 (79)	20339	
4912·9	6	20348	2, 2 (79)	20346	20347·8
4905·9	2	20377	15, 8 (79)	20380	
*4894·8	6	20424	1, 1 (81)	20422	
4882·5	7	20475	3, 2 (79)	20476	20476·7
4872·8	4	20516	5, 3 (79)	20519	
4866·7	7	20542	7, 4 (79)	20545	
4864·5	5	20551	2, 1 (79)	20554	20555·3
4852·7	7	20601	4, 2 (79)	20603	20600·9
4844·1	6	20637	6, 3 (79)	20637	
4839·2	5	20658	17, 7 (81)	20660	
4833·6	6	20682	3, 1 (79)	20684	20683·3
4816·8	†	20754	9, 4 (79)	20753	
4804·3	6	20809	4, 1 (79)	20810	20809·9
4794·7	4	20850	10, 4 (79)	20848	
4774·2	5	20940	14, 5 (79)	20938	

* The following bands were measured on Fuess Spectrogram.

† Masked by Br line 4816·7.

TABLE I (*Contd.*)

λ in A	Int.	Observed ν in cm.[1]	Assignment v', v''	Calcu- lated ν	Morgan's value
4757·5	3	21013	4, 0 (81)	21015	21015·9
4749·8	2	21047	6, 1 (81)	21047	21047·6
4729·9	3	21136	5, 0 (81)	21137	21135·6
4703·5	2	21254	6, 0 (81)	21254	21254·1
4702·3	2	21260	6, 0 (79)	21260	21258·0
4678·5	6	21368	7, 0 (81)	21367	21365·7
4655·3	5	21474	8, 0 (81)	21474	21473·1
4633·6	4	21575	9, 0 (81)	21575	21574·2
4612·1	2	21676	10, 0 (79)	21676	21678·1
4595·1	0	21756	11, 0 (81)	21756	21756·0

VIBRATIONAL ANALYSIS

As the two isotopes of bromine (Br^{79} and Br^{81}) occur in the ratio of 50·57 : 49·43, one may expect the intensities of the corresponding bands to be nearly the same. In fact, in BiBr two band systems have been observed even earlier for each of the two isotopes of bromine (Morgan). In the shorter wavelength region of the spectrum, this isotope effect gives the bands a double headed appearance. An analysis by the usual procedure (Herzberg, G., 1950) shows that all the band heads observed could be fairly well represented within ± 3 cm.$^{-1}$ by means of the following formulæ:

$$Bi^{209} \; Br^{79} \; \nu_{head} = 20532 + [135 \cdot 91 \; (v' + \tfrac{1}{2}) - 0 \cdot 534 \; (v' + \tfrac{1}{2})^2 - 0 \cdot 103$$
$$(v' + \tfrac{1}{2})^3] - [209 \cdot 50 \; (v'' + \tfrac{1}{2}) - 0 \cdot 466 \; (v'' + \tfrac{1}{2})^2]$$

$$Bi^{209} \; Br^{81} \; \nu_{head} = 20532 + [134 \cdot 69 \; (v' + \tfrac{1}{2}) - 0 \cdot 524 \; (v' + \tfrac{1}{2})^2 - 0 \cdot 1002$$
$$(v' + \tfrac{1}{2})^3] - [207 \cdot 61 \; (v'' + \tfrac{1}{2}) - 0 \cdot 458 \; (v'' + \tfrac{1}{2})^2]$$

It is interesting to note that these formulæ are exactly identical with those given by Morgan and no need was necessary to alter the vibrational constants for explaining in a satisfactory manner all the observed bands. As has been pointed out by Morgan earlier, the coefficient of the cubic term is large for the upper level and this is necessary to explain the rapid convergence of the band heads. The isotope effect was observed in about 87 bands, and their vibrational quantum numbers, observed shift and the theoretically expected shift on the basis of the band head formulæ given earlier are listed in Table II. The expression for $BiBr^{81}$ is related to that of $BiBr^{79}$ by means of the known formula (Herzberg, G., 1950).

TABLE II

Vibrational isotope effect in BiBr bands

Assignment v', v''	Observed Shift in cm.$^{-1}$	Theoretical Shift in cm.$^{-1}$
12, 27	38	38
13, 27	38	38
15, 27	40	40
12, 26	40	36
13, 26	37	36
1, 18	30	30
10, 23	66	68
14, 15	132	136
9, 22	34	31
1, 17	29	30
10, 22	27	30
11, 22	28	29
9, 21	27	28
12, 22	29	30
17, 23	57	63
19, 23	60	60
7, 19	27	25
1, 15	26	25
12, 21	32	29
17, 22	36	35
9, 19	24	24
4, 16	23	23
15, 21	35	31
2, 14	23	22
1, 13	24	22
0, 12	23	21
8, 17	22	22
2, 13	21	20
4, 14	21	21
1, 12	20	20
6, 15	22	21
0, 11	21	20
2, 12	18	19
1, 11	20	19
12, 17	25	22
0, 10	18	18
13, 17	18	22
14, 17	21	23
4, 12	18	18
1, 10	19	17
6, 13	20	18
0, 9	16	16

TABLE II (*Contd.*)

Assignment v', v''	Observed Shift in cm.$^{-1}$	Theoretical Shift in cm.$^{-1}$
13, 16	23	21
19, 17	32	31
2, 10	17	16
1, 9	16	16
8, 13	18	16
0, 8	16	15
1, 8	16	14
6, 11	14	14
0, 7	14	13
13, 14	16	18
2, 8	14	12
6, 10	15	12
0, 6	11	11
19, 14	22	26
5, 9	8	11
2, 7	12	11
4, 8	10	11
1, 6	6	10
16, 13	19	19
3, 7	7	9
0, 5	11	9
5, 8	7	10
11, 11	16	12
2, 6	8	9
1, 5	9	9
6, 8	9	8
8, 9	11	10
3, 6	8	8
0, 4	7	8
11, 10	9	11
2, 5	7	7
1, 4	7	7
10, 9	11	9
3, 5	8	6
2, 4	7	6
12, 9	8	9
1, 3	4	6
17, 10	14	15
5, 5	7	4
11, 8	6	7
2, 3	4	4
15, 9	9	11
10, 7	7	5
11, 7	4	5
6, 0	6	6

$$G(v) = \rho \omega_e (v + \tfrac{1}{2}) - \rho^2 \omega_e x_e (v + \tfrac{1}{2})^2 + \rho^3 \omega_e y_e (v + \tfrac{1}{2})^3$$

where ρ^2 is the ratio of the reduced masses of $Bi^{209}Br^{79}$ and $Bi^{209}Br^{81}$. But, some of the bands attributed to $Bi^{209}Br^{79}$ may easily well be due to $Bi^{209}Br^{81}$ of different v' and v'' values and both possibilities have been indicated in Table I. This view is further supported by the fact that the intensities of such bands are slightly higher than the isotopic counterpart of each of them separately. The intensity distribution observed in emission is in agreement with what is to be expected from the absorption spectrum reported by Morgan and the most intense bands lie on a wide open Condon parabola. Thus the close agreement of the observed and calculated isotopic displacements on the one hand and the coincidence of the absorption bands found by Morgan for BiBr with the corresponding emission bands on the other convince us that the band system observed now is the A→X system of BiBr. Also the fact that the B→X system, though feebly developed, occurs in the same region as recorded by Morgan in absorption shows that the present system can be safely attributed to the BiBr molecule.

DISSOCIATION ENERGY AND DISSOCIATION PRODUCTS

A spectroscopic determination of the heat of dissociation of a molecule obviously requires a precise knowledge of the energy of the dissociation limit above the ground state as well as the products of dissociation at this limit. Often the systems do not converge rapidly enough for an accurate determination of the dissociation limit and extrapolation methods have to be resorted to. Fortunately, the convergence of the excited levels of the A-system of BiBr is sufficiently rapid and Morgan calculated from band head formula the limit as about 4520 Å. In view of the larger number of bands observed in emission now, the dissociation energy for the upper state was evaluated more accurately by plotting a graph between $\triangle G$ and v and the improved value came out as 0·19 ev. If we add to this, the electronic excitation energy corresponding to 20495 cm.$^{-1}$ (v_{00}), *viz.*, 2·54 e.v. we find the dissociation energy of the upper state D'_e to be 2·74 ev. (including zero-point energy) and the corresponding convergence limit at $\lambda 4513·6$ is close to the value estimated by Morgan. On the other hand, the dissociation energy of the excited state of the B-system of BiBr (Morgan, *loc. cit.*) when corrected by using the current conversion factor (1 ev. = 8068·3 cm^{-1}; Herzberg, 1950) comes out to be 4·12 ev. Since the convergence is rapid here also this value can be taken to be close to the true value. Thus the difference between the dissociation energies of the excited states of the A and B systems is 1·38 ev. Since both these systems have the same lower state, namely the ground state

X, this difference in energy most probably corresponds to the difference in the excitation energies of the dissociation products of both these states. In Table III the probable products and the corresponding energies referred to the ground levels of Bi and Br atoms have been given. A scrutiny suggests that in the excited state A, BiBr possibly dissociates into the normal atoms, viz., Bi ($^4S_{3/2}$) and Br ($^2P_{3/2}$) and in the state B with Bi in the excited state ($^2D_{3/2}$).

TABLE III

Atomic excitation

Component atoms and levels	Energy in ev.*
Bi ($^2D_{3/2}{}^0$) + Br ($^2P_{3/2}{}^0$)	1·4
Bi ($^4S_{3/2}{}^0$) + Br ($^2P_{1/2}{}^0$)	0·45
Bi ($^4S_{3/2}{}^0$) + Br ($^2P_{3/2}{}^0$)	0

* Values calculated from data on *Atomic Energy States*, Bacher, R. F. and Goudsmit, S., McGraw Hill Book Co., Inc., 1932.

Thus the situation appears to be very similar to what has been observed in the case of the upper state of the well-known visible iodine absorption bands and analogous bands of bromine. The low value of the dissociation energy in the upper state of the A→X system, namely 0·19 ev., indicates that the influence of the electric field along the axis on the electron orbitals is not large enough to break the coupling between L and S of the component atoms and it appears therefore quite likely that the appropriate coupling is of Hund's case (c) type. This is supported also by a calculation of the ratio of the r_e values in the two states using the relation due to Birge and Mecke, *i.e.*, $r^2{}_e \omega_e = $ constant. From the known ω_e' and ω_e'' values one may expect the r_e' value to be about 25% more than the ground state. In BiCl where Hund's case (c) coupling has been established (Khanna, *loc. cit.*), the observed increase in the upper state is only about 7%. The fact that the (0, 0) band is not excited in the A-system of BiBr, both in emission and in absorption and that the bands themselves are all red-degraded, show that the r_e value in the upper state is much larger than in the ground state and that the coupling is in all probability of Hund's case (c) type. In the light of the Franck-Condon principle, the observation of the extension of the band system in emission only can be understood.

Another interesting feature to which attention may be drawn is the fact that the linear extrapolation method yields a value of 2·91 ev. as the dissociation energy of the lower state, which is also the ground state of the molecule. It is true that such an extrapolation is justified only for non-poplar molecules and may also lead to wrong values in the case of the excited states of molecules containing an atom with high electron affinity such as a halogen (Gaydon, A. G., 1947). But in the ground state, the linear extrapolation may probably give a value 25% larger than the true value (Herzberg, G.) and so the value of 2·91 ev. should be regarded as an upper limit. The lower limit naturally may be taken to be the energy of the highest vibrational level observed in that state; in this case it is 0·68 ev. ($v'' = 28$). If, however, the value of 2·91 ev. turns out to be close to the true dissociation energy of the ground state, then one is forced to conclude that the excess for the state X over A, in view of the energy difference of 0·45 ev. between the $^2P_{1/2}$ and $^2P_{3/2}$ levels of bromine, may be due to the molecule dissociating in the lower state into Bi ($^4S_{3/2}$) and Br ($^2P_{1/2}$) atoms.

ELECTRONIC TRANSITION INVOLVED

In considering the molecular states that can arise from a combination of the atoms, it is often adequate to consider the outermost electrons of the constituent atoms. The ground state electronic configuration of the two atoms in the present case are

Bi ($KLMNO_{spd}$) $6s^2$ $6p^3$ ($^4S_{3/2}$)

Br (KLM) $4s^2$ $4p^5$ ($^2P_{3/2}$)
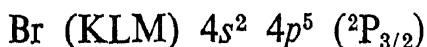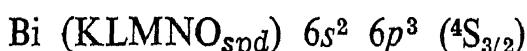
where O_{spd} represents the O shell in which only the s, p, and d sub-shells are filled. The electronic terms that can be derived from the ^4S and the ^2P states are $^3\Sigma^-$, $^3\Pi$, $^5\Sigma^-$ and $^5\Pi$. But to decide as to which of these are low lying, one may, as has been done by Khanna, B. N. (*loc. cit.*), consider the levels of the molecule NF. N and F belong to the same groups in the periodic table as Bi and Br respectively and so their electronic terms will be similar. In the 'united atom' model, sulphur with its 16 electrons corresponds to the "united atom" for the NF molecule and the states derivable from a sulphur atom in its low lying states $^3P_{2, 1, 0}$ are $^3\Sigma^-$ and $^3\Pi$. Hence these two states may be expected to lie lowest for BiBr molecule and we may therefore leave out of further consideration the higher multiplicity terms.

By analogy with the molecule BiCl and in view of the much larger r_e' value in the excited state, here also the reasonable coupling appears to be of Hund's case (c). The appropriate Ω values for Bi ($^4S_{3/2}$) + Br ($^2P_{3/2}$) are therefore $\Omega = 3, 2 (2), 1 (3)$ and $0 (4)$, where the numbers in parenthesis indicate the

number of states of the type given. For $\Omega = 0$ the different states are 0^+, 0^+, 0^-, 0^-. On the other hand, the higher dissociation energy for the lower state would seem to indicate in that state either Hund's case (a) or case (b) or any intermediate coupling. A correlation of the states by standard methods (Herzberg, *loc. cit.*) shows that 0^+ state corresponds to $^3\Sigma^-$ state. Similarly the atoms Bi ($^4S_{3/2}$) and Br (^2P) can give rise to an upper $^3\Pi$ (0^+) state. In molecular orbital notation, the transition involved in the A $\to$ X system under study may therefore be represented by

$$(z\sigma)^2 \, (y\sigma)^2 \, (x\sigma)^2 \, (\omega\pi)^4 \, (v\pi) \, (u\sigma): \, ^3\Pi \, (0^+) \to (z\sigma)^2 \, (y\sigma)^2 \, (x\sigma)^2 \, (\omega\pi)^4 \, (v\pi)^2: \, ^3\Sigma^-$$

where the symbols have their usual significance (Mulliken, R. S., 1932; Coulson, C. A., 1959). $v\pi$ represents an antibonding orbital of the type ($6p\pi_{Bi} - 4p\pi_{Br}$) and $u\sigma$ an antibonding orbital of the type ($6p\sigma_{Bi} - 4\sigma p_{Bi}$). The reasons for not considering other possible states and allowed transitions have been discussed in detail by B. N. Khanna (*loc. cit.*) for BiCl and will not be given here as those arguments can equally well be used for BiBr. The bond order is seen to be 2 in both states of BiBr (A-system) and so they may be expected to have dissociation energies of the same order of magnitude. But our knowledge of the ordering of the energies of molecular orbitals arising from high quantum atomic orbitals is still meagre; if one assumes that $u\sigma$ is above $v\pi$ as in the molecular orbitals arising from atomic 2 quantum orbitals then there is some rough theoretical justification for the linear extrapolated value of higher dissociation energy for the ground state of BiBr. This simple argument will then fail to account for the converse observation in BiCl. However, both facts can be reconciled if we suppose, as suggested earlier, that in BiBr in the ground state dissociation takes place with Br in the higher multiplet level $^2P_{1/2}$. Since in the correlation of the atomic and the molecular states, multiplet splittings are ignored, it is not possible to establish unambiguously if that is so. A more precise experimental determination of the dissociation energy in the ground state of BiBr will therefore be of interest.

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SUMMARY

The emission spectrum of bismuth monobromide has been investigated and a vibrational analysis of the A$\to$X system has been made. About 286 bands were recorded in the region $\lambda\lambda$ 4595–6063 and the isotope effect due to Br[79] and Br[81] was observed in about 87 bands. A value of $2 \cdot 74$ ev. for the

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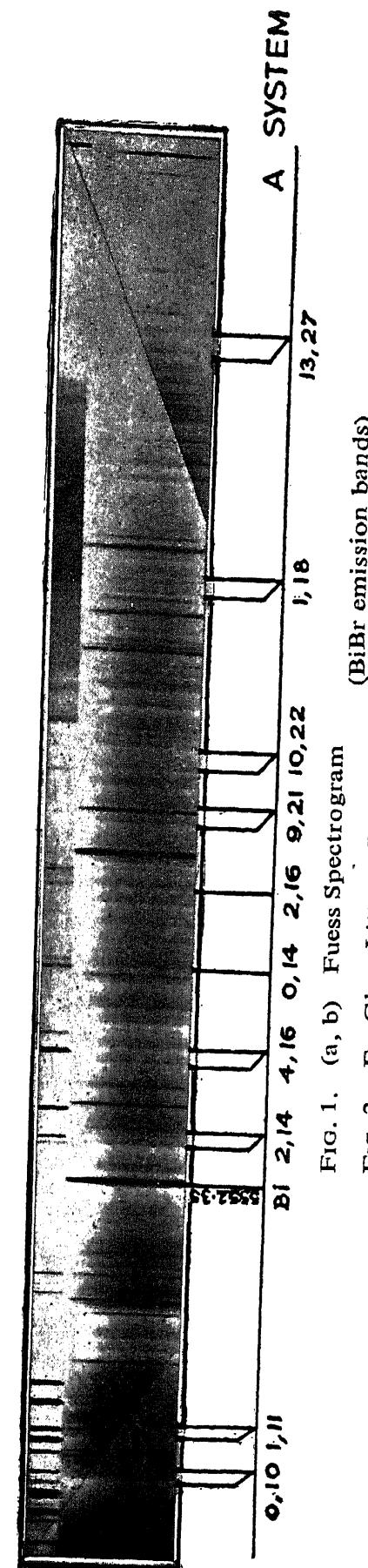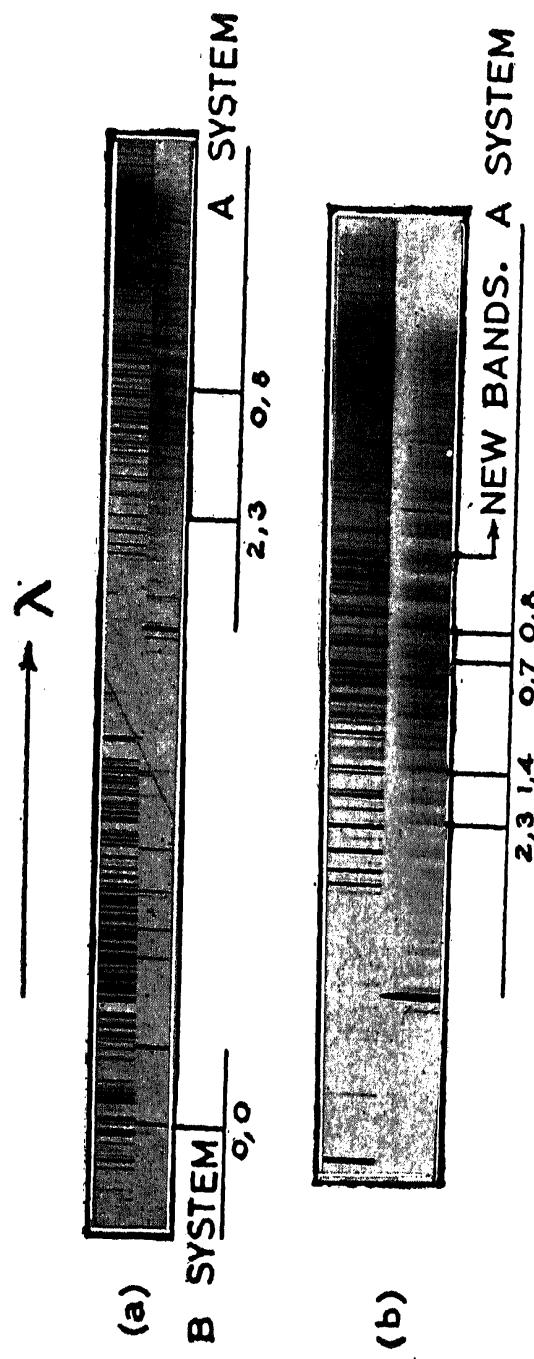
FIG. 1. (a, b) Fuess Spectrogram   (BiBr emission bands)

FIG. 2. E₁ Glass Littrow Spectrogram

dissociation energy of the excited state has been obtained and arguments have been given to show that the dissociation products in the excited state are Bi $(^4S_{3/2})$ and Br $(^2P_{3/2})$ and that those of the ground state are most probably Bi $(^4S_{3/2})$ and Br $(^2P_{1/2})$ atoms.

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