

Ultraviolet bands of mercury bromide

By

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With 1 figure in the text

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The ultraviolet bands of mercury bromide have been excited in uncondensed discharge and photographed with a quartz Littrow spectrograph. The class II system, lying between λ 2900 Å to 2700 Å, suggested by WIELAND as due to the triatomic molecule, has been studied in detail and ascribed to the diatomic molecule. The bands in the region λ 2900 Å to 2770 Å have been analysed into two systems which may form the two components of a ${}^2\Pi - {}^2\Sigma$ electronic transition with a ${}^2\Pi$ interval equal to 969.4 cm^{-1} .

Another system most probably due to ${}^2\Sigma - {}^2\Sigma$ has been observed in the region λ 2770 to 2720.

1. Introduction

The present investigation is in continuation of the author's work on the mercury chloride bands which have been recently analysed and the results were presented in this Journal¹. The first extensive work on the band spectrum of mercury bromide was done by WIELAND²⁻⁴. He divided the bands between λ 7000 and 2300 into three classes. The class I bands extending from λ 2670 to 2430 and degrading to the violet were ascribed to the diatomic molecule HgBr. WIELAND derived the following formula for $\text{Hg}^{202}\text{Br}^{81}$:

$$v = 38574.4 + 228.5 u' - 186.25 u'' - 0.950 u'^2 + 0.975 u''^2.$$

The class II bands lying between λ 2900 and 2700 and also degrading to the violet were ascribed to the triatomic molecule HgBr_2 on account of the complexity of the appearance of the bands. Most of the vibrational bands were resolved and WIELAND gave wavelength data for the first and other rotational members of these bands. But no analysis was given by him. The class III bands are diffuse and complex and occur in the longer wavelength region between λ 5000 and 3200. WIELAND gave a complete vibrational analysis only for the class I² and class III⁴ systems.

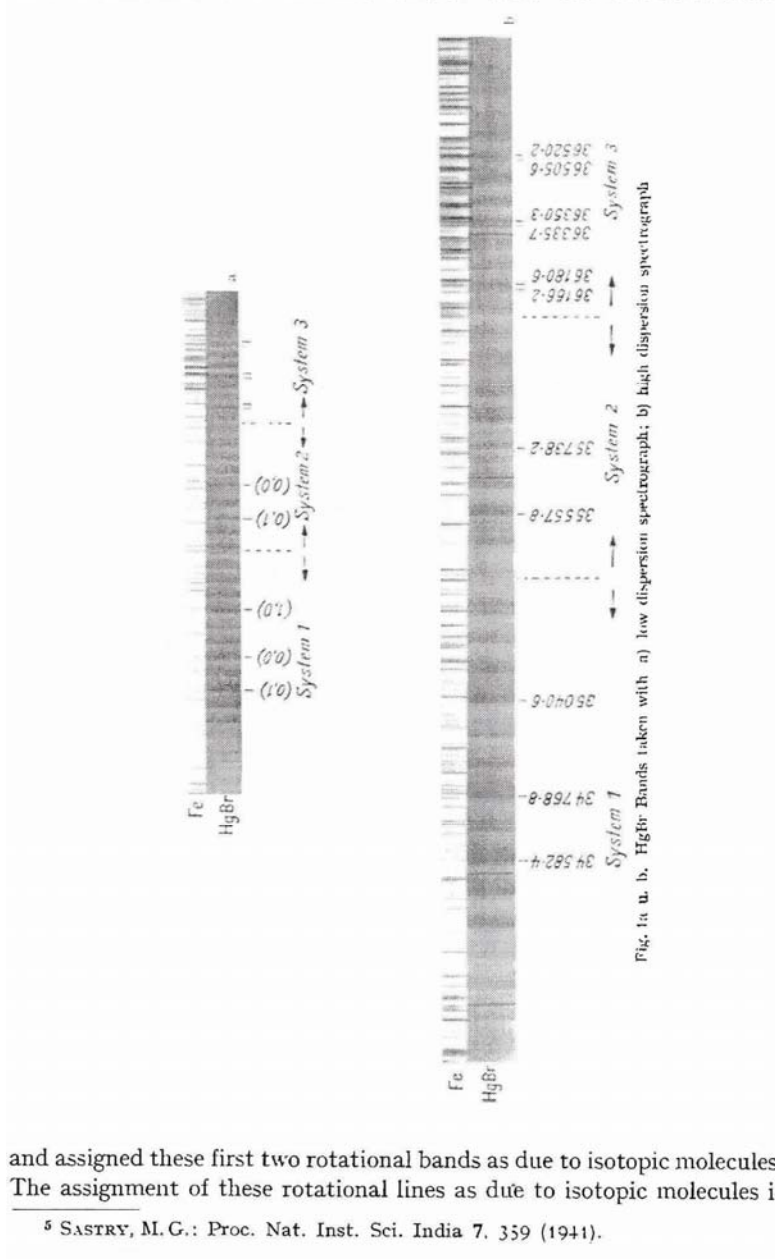
¹ KRISHNAMURTHY, V.G.: Ultraviolet bands of mercury chloride. Z. Physik **150**, 287 (1958).

² WIELAND, K.: Helv. phys. Acta **2**, 46, 77 (1929).

³ WIELAND, K.: Z. Physik **77**, 157 (1932).

⁴ WIELAND, K.: Helv. phys. Acta **12**, 295 (1939).

Later SASTRY⁵ studied class II bands and gave wavelength data for the first and second rotational members of most of the vibrational bands



and assigned these first two rotational bands as due to isotopic molecules. The assignment of these rotational lines as due to isotopic molecules is

⁵ SASTRY, M.G.: Proc. Nat. Inst. Sci. India 7, 359 (1941).

incorrect. The vibrational constants obtained by SASTRY for the band heads of $\text{Hg}^{202}\text{Br}^{81}$ are

$$\begin{aligned}\omega'_e &= 459.0 & \alpha_e \omega'_e &= 3.6 \\ \omega''_e &= 372.3 & \alpha_e \omega''_e &= 3.8 \\ \nu_e &= 34537.8 \text{ cm}^{-1}.\end{aligned}$$

The vibrational constants obtained by SASTRY for these bands do not show any level in common with the vibrational constants obtained by WIELAND for the farther ultraviolet system (class I) and there is no correlation between these two systems.

A reinvestigation of the band spectrum of mercury bromide was therefore called for and the results obtained are given below.

2. Experimental

The experimental arrangement and the method of excitation of the spectrum are essentially the same as those adopted in the case of mercury chloride bands¹. The discharge was intense blue and the bands could be excited much more easily than in the case of mercury chloride bands. Photographs were taken with a Hilger medium and Littrow spectrographs. The exposures extended from half to three hours. The plates were measured using a Hilger comparator and reduced to wavelengths using iron arc standards.

3. Results

The spectrum of the mercury bromide bands is reproduced in plate. The bands are violet degraded. The bands on the long wavelength side have somewhat sharper edges, getting diffuse and broad towards shorter wavelengths. Particularly in the lower wavelength region, the bands are very diffuse and several bands are headless.

Table 1 gives the wavenumbers and intensities of the bands obtained in the present investigation. Columns 3 and 4 give the system and the classification of the bands.

4. Discussion

In the present investigation, a fairly large number of new bands has been recorded in addition to those already recorded by WIELAND. A system appearing in transformer discharges and also in high frequency discharges cannot, in general, be due to a triatomic molecule because of the highly disruptive nature of these discharges. The bands are therefore assigned to diatomic molecule and are analysed as such in the present investigation. It has been found that the bands in the

longer wavelength region, λ 2930 to λ 2835, are simple and normal in appearance. The bands in the region λ 2900 to 2860 are very intense and the (0, 0) band may occur in this region. Several bands in this region are tried as (0, 0) bands and finally it is found that with 34768.8cm^{-1} as the (0, 0) band, all the bands in this region upto λ 2835 could be satisfactorily assigned. But an unexpected difficulty arises when we

Table 1. *HgBr Bands*

Wave Number cm^{-1}	Intensity	System	Classification ($v' v''$)	Wave Number	Intensity	System	Classification ($v' v''$)
34126.7	3	1	1, 5	35835.6	4	2	4, 5
215.5	3	1	0, 5	879.3	3 <i>bd</i>	2	2, 2
307.1	4	1	1, 4	955.5	3 <i>bd</i>	2	3, 3
398.0	5	1	0, 2	990.4	3	2	1, 0
487.0	6	1	1, 3	36002.1	3	3	—
582.4	7	1	0, 1	029.3	3 <i>bd</i>	—	—
670.0	7	1	1, 2	106.1	3 <i>bd</i>	3	—
768.8	8	1	0, 0	119.8	3	3	—
857.3	6	1	1, 1	166.2	5	3	—
942.6	5	1	2, 2	180.6	5	3	—
35038.1	6	1	1, 0(<i>P</i>)	223.8	4	3	—
040.6	7	1	1, 0	238.3	4	3	—
120.6	6 <i>bd</i>	1	2, 1	277.7	3 <i>bd</i>	3	—
202.2	5	1	3, 2	292.2	3	3	—
280.4	5	1	4, 3	335.7	5	3	—
310.3	4 <i>bd</i>	1	2, 0	350.3	5	3	—
359.7	3 <i>bd</i>	1	5, 4	391.3	4	3	—
391.6	5	2	0, 2	405.9	4	3	—
444.3	2 <i>bd</i>	2	1, 3	451.0	2 <i>bd</i>	3	—
477.0	5	1	4, 2	465.6	2	3	—
557.8	6	2	0, 1	505.6	4	3	—
630.0	5	2	1, 2	520.2	4	3	—
708.9	3 <i>bd</i>	2	2, 3	560.3	3	3	—
738.2	6	2	0, 0	575.0	3	3	—
774.1	3 <i>bd</i>	2	3, 4	613.9	2 <i>bd</i>	3	—
809.9	6	2	1, 1	628.6	2	3	—

consider the bands in the region below λ 2835. The bands in the region λ 2835 to 2770 are very much crowded giving a complex appearance to the spectrum in this region. The analysis of the bands in this region presented considerable difficulty. All these bands could not be assigned as forming part of the above system. It has been found that the complexity of the bands in this region is due to superposition of another band system and all the bands in this region could be assigned only if most of these are considered as forming part of a second system with the (0, 0) band at 35738.2cm^{-1} .

The band heads of these two systems are shown in diagonal arrays in Tables 2 and 3 respectively.

The following vibrational constants have been derived for these two band systems.

For the longer wavelength system

$$\nu = 34724.3 + 275.8u' - 186.1u'' - 2.1u'^2 + 0.6u''^2.$$

For the shorter wavelength system

$$\nu = 35702.6 + 254.3u' - 183.0u'' - 1.3u'^2 + 1.0u''^2.$$

Table 2. HgBr Bands. System 1

ν'	ν''					
	0	1	2	3	4	5
0	34768.8 271.8	186.4 34582.4 274.9	184.4 187.0	34398.0 272.3	182.5 183.3	34215.5 271.5
1	35038.1 (P) 35040.6 269.7	183.3 34857.3 263.3	187.0 178.0	34670.3 272.3	183.3 34487.0	179.9 34307.1 180.4 34126.7
2	35310.3	189.7 35120.6	178.0	34942.6 259.6		
3				35202.2		
4				35477.0	35280.4	
5						35359.7

Table 3. HgBr Bands. System 2

ν'	ν''					
	0	1	2	3	4	5
0	35738.2 252.4	180.4 35557.8 251.1	166.2	35391.6 238.4		
1	35990.4	180.5 35809.9	179.9	35630.0 249.3	185.7	35444.3 264.6
2				35879.3	170.4	35708.9 246.6
3						181.4
4					35955.5	35774.1 35835.6

The lower state frequencies of these two systems are nearly equal and equal to the lower state frequency of the farther ultraviolet system occurring at λ 2665 to 2470. These two band systems may form the two components of a $^2\Pi - ^2\Sigma$ electronic transition in which the $^2\Pi$ separation will be 969.4 cm^{-1} which compares well with the corresponding value 838.7 cm^{-1} obtained in the case of mercury chloride. On the other hand, if the first system and the farther ultraviolet system (λ 2665 to 2470) form the two components of a $^2\Pi - ^2\Sigma$ transition, the $^2\Pi$ interval will be 3827.7 cm^{-1} .

The bands from λ 2792 to 2770 are weak, broad and diffuse. The appearance and intensity of the bands suddenly change from λ 2764 onwards towards the shorter wavelengths. In the region λ 2770 to 2725, three pairs of intense bands occur at

	169.5	169.9	
ν	36166.2	36335.7	36505.6
	14.4	14.6	14.6
	36180.6	36350.3	36520.2
			cm ⁻¹

The separations of these three pairs are equal, being 14.5 cm⁻¹ and the intervals between these groups are nearly 170 cm⁻¹. Several other pairs

Table 4. *HgBr Bands. System 3*

	169.9		169.5		164.1				
36505.6		36335.7		36166.2		36002.1			
14.6		14.6		14.4					
36520.2		36350.3		36180.6					
		224.6		225.1		221.7			
			169.0		167.5				
		36560.3		36391.3		36223.8			
		14.7		14.6		14.5			
		36575.0		36405.9		36238.3			
				222.6		227.2			
				36613.9	162.9	36451.0	173.3	36277.7	171.6
				14.7		14.6		14.5	36106.1
				36628.6		36465.6		36292.2	13.7
									36119.8

of bands with almost the same separation occur in this region. These bands cannot form part of the second system analysed above, nor can they form part of the farther ultraviolet system at λ 2665 to 2470. The two members of the several pairs of these bands are almost equal in intensity and the separations of the members of each pair are almost constant. The two members of these pairs cannot be due to isotopic molecules for if they are so, the separations will not be constant, as is in the present case but will vary from pair to pair. These bands appear unique and the disposition and intensities of these bands show that these form a different system altogether.

The band heads of this system are shown in diagonal array in Table 4.

The vibrational frequencies of the lower and upper states of this system are about 171 cm⁻¹ and 225 cm⁻¹ respectively.

The electronic transition involved in these bands is most probably $^2\Sigma - ^2\Sigma$. The occurrence of a $^2\Sigma - ^2\Sigma$ transition of almost the same energy as the $^2\Pi - ^2\Sigma$ transition is expected in this region from theoretical considerations. But it has not been definitely established, so far, in any of the halides of zinc, cadmium or mercury. If the assignment of the present bands as due to $^2\Sigma - ^2\Sigma$ is correct, the band systems due to similar

transition must occur in the halides of other molecules also. Experiments in this direction are in progress.

5. Isotope effect

Bromine has two isotopes Br⁷⁹ and Br⁸¹ which have an abundance ratio 1:1. The isotopic displacement for a vibrational band (v', v'') is given by

$$\nu_v^i - \nu_v = (\rho - 1) \{ \omega'_e u' - \omega''_e u'' \}$$

where ν_v^i refers to Hg²⁰²Br⁸¹ and ν_v to Hg²⁰²Br⁷⁹. The two isotopic heads must be of equal intensity. The isotopic factor $(\rho - 1)$ comes out to be -0.0089 and using this value, the isotopic separations for (2, 0), (2, 1) and (3, 2) bands in the first system are 5.2, 3.9, and 4.7 cm⁻¹ respectively. As the isotopic separations are very small and further as most of the vibrational bands are resolved into rotational structure and some are diffuse, it has become difficult to observe the isotope effect clearly.

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