

A NEW BAND SYSTEM OF THE HgBr MOLECULE.

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(Plate VI)

ABSTRACT. A new band system of the HgBr molecule is obtained in the ultra-violet between λ_{2470} and λ_{2430} , consisting of about 20 bands, which are headless and diffuse. The three sequences $\Delta v = 0$ and ± 1 are identified. The bands are represented by the formula

$$\nu = 40720 + [166(v' + \frac{1}{2}) - 1.1(v' + \frac{1}{2})^2] \\ - [183(v'' + \frac{1}{2}) - 2.0(v'' + \frac{1}{2})^2]$$

The system is considered as due to a transition from a higher $^2\Sigma$ state to the lower ground state $^2\Sigma$, determined previously by Wieland.

INTRODUCTION

It is well-known that the diatomic halides of the elements of Group II-a of the Periodic Table give rise to band systems ascribed to transitions from a higher $^2\Pi$ or $^2\Sigma$ to a lower $^2\Sigma$ state. That the ground state is a $^2\Sigma$ has been established from experiments on the absorption of a few of the halides. Our knowledge of the similar molecules of the Group II-b elements is still far from complete. Reporting the analysis of the HgF bands, an attempt has been made by Howell (1943) to systematise and interpret the band spectra of the diatomic halides of Zn, Cd and Hg. In the light of Howell's observations, a reinvestigation of the spectra of HgCl, HgBr and HgI has been undertaken by the authors, in continuation of the work carried out by Sastry (1941 and 1942) in this laboratory.

The results obtained by us in the case of HgCl (reported briefly in *Current Science* in press) show that there are two distinct band systems of this molecule in the ultra-violet, due to transitions from two different $^2\Pi$ states to a common lower $^2\Sigma$ state, which is considered to be the ground state of the molecule, on the analogy of the other related molecules. One of the systems (lying between λ_{2900} and λ_{2700}), was analysed partially by Cornell (1938) and more completely by Sastry (1941). The separation is about 90 cms^{-1} . The other system, also due to $^2\Pi - ^2\Sigma$, has the electronic width as large as 3890 , leading to widely separated components $^2\Pi_{\frac{3}{2}} - ^2\Sigma$ and $^2\Pi_{\frac{1}{2}} - ^2\Sigma$, the former being the one designated as Class I by Wieland (1929). The latter has been established by the authors in the region $\lambda_{2900} - \lambda_{2700}$. A full discussion of these would be presented in another paper.

HgBr BANDS

In the case of HgBr as well, two band systems are known in the ultra-violet, as investigated by Wieland and by Sastry; the correlation between the two does not appear to be satisfactory. The interval between the (0, 0) bands of these two systems is 4014 cms^{-1} and agrees well with what might correspond to the electronic doublet width, expected for this molecule on the basis of

Howell's suggestion. But the constants obtained for the two systems indicate no common level.

Table I shows a comparison of the vibrational constants for the ground states of HgF and HgCl (in cms^{-1}).

TABLE I.

Molecule	ω''	$x''\omega''$
HgI'	490.8	4.05
HgCl	293.4	1.82
HgBr	W186.25 S372.3	W0.975 S3.8

For HgBr the upper values marked W are those derived by Wieland and the lower by Sastry, for the two different systems. The upper value is in conformity with that expected to be the normal state of HgBr. The lower value, if it proves to be real, must correspond to a $^2\Sigma$ state, different from the ground state of this molecule.

A reinvestigation of the HgBr bands, to bring them, if possible, into conformity with the HgCl bands mentioned above, is considered desirable. With this aim, the spectrum has been photographed again under different temperature and pressure conditions, using the same source as that employed by Sastry previously. Particular attention is paid to examine the variations, if any, in the intensity distribution among the bands leading to the possibility of splitting the less refrangible system into two different systems. While this work is still in progress, it has been noticed that a third band system is emitted by the HgBr molecule in the ultra-violet region, which was just mentioned by Sastry. The purpose of the present paper is to present details of these new bands. They occur between λ_{2470} and λ_{2430} , under the same conditions as the two previously known ultra-violet systems of HgBr. They are absent in discharges through vapours of various other salts, such as HgCl, HgI, HgO, HgS, etc.

Plate VI is a reproduction of the bands. They are headless and somewhat diffuse. Twenty-two of these could be measured on the high dispersion plates taken with Hilger E. 1 Quartz Littrow Spectrograph (2.5 A per mm.).

Three well separated sequences, $\Delta v = 0$ and ± 1 , ascribed to a single system, have been identified, the sequence degradation of the bands being towards the less refrangible side. Table II gives the wave-lengths, intensities and wave-numbers of the bands and the last column shows the classification. The wave-numbers are given only to the nearest integer, as no greater accuracy can be obtained, on account of the nature of the bands, although the dispersion of the spectrograph is high.

In any single sequence, the band head intensity rises to a maximum and then falls off. Table III gives the intensity distribution arranged in the usual diagonal array. The intensities are visual estimates.

TABLE II
HgBr Bands

Wave-length	(Int.)	Wave-number	Classification (v' , v'')
2469.5	(0)	40481	(6, 7)
2468.8	(2)	40493	(5, 6)
2468.3	(0)	40501	(4, 5)
2467.8	(2)	40509	(3, 4)
2467.3	(4)	40518	(2, 3)
2466.9	(1)	40525	(1, 2)
2466.4	(2)	40533	(0, 1)
2459.5	(1)	40646	(5, 5)
2458.5	(2)	40663	(4, 4)
2457.8	(3)	40675	(3, 3)
2457.0	(4)	40687	(2, 2)
2456.7	(2)	40693	(1, 1)
2455.6	(2)	40711	(0, 0)
2452.4	(2)	40764	(8, 7)
2451.2	(2)	40784	(7, 6)
2450.3	(2)	40799	(6, 5)
2448.8	(3)	40824	(5, 4)
2448.1	(4)	40835	(4, 3)
2447.5	(3)	40846	(3, 2)
2446.5	(1)	40862	(2, 1)
2445.9	(0)	40873	(1, 0)
2437.7	(2)	41010	(4, 2)

TABLE III
Intensity Distribution

v' v''	0	1	2	3	4	5	6	7
0	2	2
1	0	2	1
2	...	1	4	4
3	3	3	2
4	2	4	2	0
5	3	1	2	...
6	2	...	0
7	2	...
8	2

The (0, 0) band is not the most intense in the system, the parabola being displaced and analogous to what is obtained in the Si N. bands (Jevons' Report, p. 66). An alternative analysis would be to consider the most intense band in each sequence as the first Q head in the sequence and regarding the fainter bands as the component P heads. This would give ω'' a value of about 172 cms^{-1} , differing much and probably beyond observational error from Wieland's value $\omega'' = 186.25$ for the ground $^2\Sigma$ state of the HgBr molecule shown in Table I. With the classification adopted here, $\omega'' = 183$. This agreement is regarded also as lending support to the assignment of the bands to the HgBr molecule.

Further confirmation from isotope shifts could not be obtained as the shifts are small and the band heads are diffuse.

The following formula has been calculated which represents the wave-numbers of the band heads approximately.

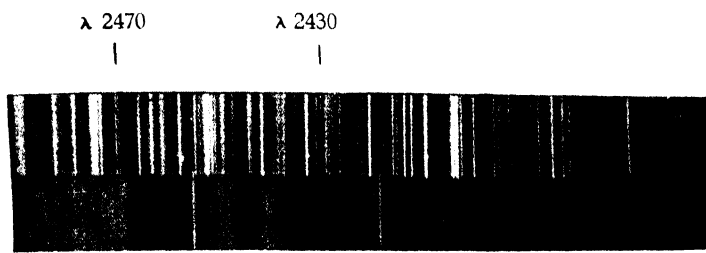
$$\begin{aligned} \nu = & 40720 + [166(v' + \frac{1}{2}) - 1.1(v' + \frac{1}{2})^2] \\ & - [183(v'' + \frac{1}{2}) - 2.0(v'' + \frac{1}{2})^2] \end{aligned}$$

The system probably arises from the transition ${}^2\Sigma - {}^2\Sigma$, the lower one being the normal state of the molecule.

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REFERENCES

- Cornell (1938), *Phys. Rev.*, **54**, 341.
Howell (1943), *Proc. Roy. Soc.*, **A**, **182**, 95.
Sastry (1941), *Proc. Nat. Inst. Sci. Ind.*, **7**, 351 and 359.
" (1942), " " " " " **8**, 289.
Wieland (1929), *Helv. Phys. Acta.*, **2**, 46 and 77.
" (1932), *Zeit. f. Phys.*, **77**, 157.



$\Delta\nu$ | | |
 Hg₂
 -1 0 +1
Band Spectrum of HgBr.
Fig. A