

ULTRA-VIOLET BAND SYSTEMS OF THE MERCURY IODIDE MOLECULE.—PART I

BY K. R. RAO,* M. G. SASTRY AND V. G. KRISHNAMURTI

(Plate VII)

ABSTRACT. The ultra-violet bands of the mercury iodide, excited in a discharge tube, are photographed with a Hilger large quartz Littrow spectrograph. The systems C and D lying in the regions $\lambda_{3100}-\lambda_{2800}$ and $\lambda_{2800}-\lambda_{2650}$ are measured. The wavelengths of the C system are compared with those published by Wieland, the data obtained in the system D being entirely new. Analysis of the two systems have led to the following vibrational constants—

	ν_c	ω'	$x'\omega'$	ω''	$x''\omega''$
System C :	32730.9	235.6	2.16	125.9	1.07
System D :	36269.2	178.0	1.14	125.7	1.10

They are in agreement with the values determined approximately by Wieland from the study of fluorescence of HgI. The origin of the D system is, however, different from that suggested by Wieland. With the classification obtained in the present work, the systems could be attributed to the two components of a $n^2\pi-2\Sigma$ electronic transition with a 2Π interval of 3538 cm^{-1} which is shown to be in conformity with the corresponding intervals obtained for the other mercury halides, HgI² and HgCl.

INTRODUCTORY

The mercury iodide molecule has an extensive band spectrum in the ultra-violet. Wieland (1929) investigated these bands with a grating having a dispersion of 10A. per mm. in the first order and quartz spectrographs of nearly the same dispersion at λ_{2500} . The systems reported by him are shown in Table I, together with those observed by later investigators, Prilheshejewa (1932) and Sastry (1942)

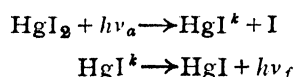
TABLE I

Author	Region	Previous designation	Present designation
Wieland	4500-3400	Class III	B
.....	3100-2800	" II	C
.....	2800-2650?	" I	D
.....	2700? 2530	E
Sastry	2500-2530	Class A	F
Prilheshejewa	2240-2168	G
.....	2160-2114	H

In his earlier work Wieland *loc. cit.* investigated these bands in emission but the wavelength data were given only for the system C. Although no analysis

*Fellow of the Indian Physical Society.

was presented, certain regularities were indicated among the bands of this system and the bands themselves were ascribed to the triatomic molecule HgI_2 . In later work, studying the absorption and fluorescence of the vapour of mercury iodide, Wieland (1932) ascribed these bands to the diatomic molecule. By optical excitation of the vapour by sparks from different metals and using suitable filters, fluorescence spectra were obtained which were associated with the equations



where the difference $(hv_a - hv_f) \geq$ the dissociation energy of $\text{HgI}_2 \longrightarrow \text{HgI} + \text{I}$. The fluorescent systems were measured and from a study of their structure, the following approximate formulæ were suggested,

$$\text{System C: } \nu = 32784 + [233.3\nu' - 2.25\nu'^2] - [124.0\nu'' - 1.0\nu''^2]$$

$$\text{System D: } \nu = 36130 + [175\nu' - 120\nu'']$$

For system B no analysis was given but the occurrence of the wave number intervals 120 and 180 was mentioned, which is suggestive of the probable electronic transition involved in their emission.

One of the writers (Sastry, 1942) published the wavelength data of the system E obtained in emission with a Hilger E_1 quartz Littrow spectrograph and in addition obtained a new system between $\lambda\lambda 2530-2560$ (designated by him as class A but hereafter will be referred to as system F in conformity with the designation of the other systems). The system E was found by him to consist of two components α_1 and β_1 having a common final state and an electronic width of about 766 cm^{-1} . The system F was attributed by him to a transition ${}^2\Pi - {}^2\Sigma$ showing four component heads and an electronic separation of 126 wave number units. As was mentioned by Sastry, the analysis does not show any level in common with the other bands of HgI . In view of this, a reinvestigation seemed desirable to systematise the analysis and interpretation of all the known bands of mercury iodide and to examine if they can be correlated with the band systems of the other mercury halides.

As a first step, the systems C and D are considered in this paper, a preliminary report of which appeared in *Current Science* (in press). Both the systems are newly photographed and measured, as no wavelength data appear to have been published at all for system D and system C was obtained by Wieland with a comparatively lower dispersion instrument.

EXPERIMENTAL

The bands were excited in a pyrex discharge tube about 10 cms by 1.5 cms diameter, containing mercury iodide in a small side bulb which could be heated if necessary. The excitation was either by a quarter-kilo watt transformer giving about 15000 volt or by a small 8 inch induction coil. Continuous evacuation by a Cenco-Hyvac pump was necessary. The discharge was bright violet and could be maintained easily for hours with just occasional heating

Ultra-violet Band Systems of the Mercury Iodide Molecule 325

of the mercury iodide container. Two Hilger quartz spectrographs were used for photographing the spectrum, the measurements being made by the larger one of the Littrow type with a dispersion of 3.8Å per mm. at $\lambda 2800$. The measurements, made by a Hilger measuring micrometer, are the average of three independent settings. Iron arc lines were used as standards for determining the wavelengths.

The spectrum is shown in plate VII.

In both systems the bands on the long wavelength side have somewhat sharper edges, getting diffuse as they occur towards shorter wave lengths. At the extreme ultra-violet end, they are very crowded, exhibit no edges at all and are diffuse and mostly unresolved. In measuring the plates the micrometer settings were made against the edges of the bands where they are sharp and against the central maximum where they are diffuse. About 130 bands are measured in system D. Table 2 gives the wavelengths and wave numbers of the heads, the intensities being the usual visual estimates.

ANALYSIS

The fourth column in the Table 2 gives the assignment of the vibrational quantum numbers, as determined in the present work. About 90 bands are classified. A few of the bands are assigned twice. One difficulty met with, in working out the analysis, is the ambiguity in the possible assignment of the bands lying particularly in the extremely crowded region below about $\lambda 2700$. This makes the classifications in this part of the spectrum somewhat uncertain. There is need for photographing this region with a much higher dispersion in order to clear the ambiguities. The following formula is calculated to represent the band heads :

$$\nu = 36269.2 + [178.0(v' + \frac{1}{2}) - 1.14(v' + \frac{1}{2})^2] - [125.70(v'' + \frac{1}{2}) - 1.10(v'' + \frac{1}{2})^2]$$

For about 70 bands the "obs-calc" values are less than 3 units. The larger discrepancies in the remaining bands are believed to be due to the uncertainties in the measurement and the ambiguities in the classification referred to above.

The constants ω' and ω'' agree well with those obtained approximately by Wieland (1932) from the fluorescent system but it will be seen that the system origin is shifted towards the violet by about 160 cm^{-1} . Many of the stronger bands in emission are thereby brought into the scheme of classification. This shift is also supported by the view advanced by Howell (1943) and discussed in a later paragraph of this paper.

The intensities of the bands are shown in the usual diagonal matrix in Table 3 which contains also the values of ΔG in the upper and lower states.

The band spectra of several iodides show an intensity distribution corresponding to an open parabola. Such a definite characteristic is not seen in the present bands. The (0, 0) band is no doubt not the most intense and the stronger bands occur in the two progressions $v'=0$ and $v''=0$. There is however, an asymmetrical development of the sequences, those giving rise to bands on the

lower frequency side of the origin being very poorly developed while on the violet side long sequences are obtained for $\Delta v = +3$ to $+7$.

TABLE 2 Hg I bands. (System D)

Wavelength	Int.	Wave number	Classification (v', v'')	Obs-cal.
2808.88	3	35590.0	0,6	2,3
08.47	3	596.2
00.40	2	698.2	0,5	-0,6
00.22	2	701.0
2798.22	2	726.5	2,8	8,4
95.31	2	763.7	1,6	0,7
93.05	1	792.7
91.29	5	815.1	0,4	0,6
86.66	3	874.7	1,5	-0,8
83.81	1	911.4	5,11	-2,3
82.16	5	932.7	0,3	1,3
80.21	2	957.9	4,9	5,6
77.13	3	997.8	3,7	0,4
74.97	2	36025.8
73.05	5	050.7	0,2	0,2
72.42	3	058.9	4,8	-0,7
69.51	2	096.9
65.80	2	145.2
64.50	3	162.2	2,4	-1,5
63.77	3	171.8	0,1	0
59.64	2	226.0	1,2	0,8
57.17	2	258.6
55.60	2	279.0	2,3	-1,6
			4,6	2,4
2754.37	2	36295.3	0,0	0
51.16	1	337.8	3,4	2,9
50.46	4	346.8	1,1	-0,7
47.33	3	388.2	4,5	-1,9
45.67	2	410.2
44.29	2	428.5
43.20	...	442.7	5,6	-0,5
42.66	2	450.2	3,3	-1,6
41.17	5	469.9	1,0	-1,1
38.66	3	503.4	4,4	-0,4
37.46	2	519.4	2,1	-1,6
36.49	2	532.4
34.93	2	553.1	5,5	-2,6
33.69	2	569.8	3,2	-1,1
30.47	3	613.0
28.24	5	642.9	2,0	-1,6
26.42	4	667.3	5,4	-3,1
24.33	2	695.4
21.93	2	727.8
21.12	2	738.7	4,2	-1,1
16.90	3	795.8
15.64	5	812.9	3,0	-2,8
14.67	4	826.0	8,7	6,9
12.18	3	859.8	4,1	-1,3
11.20	3	873.1	9,8	4,6
10.38	3	884.3	7,5	2,2
09.78	3	892.4
08.98	1	903.3	5,2	3,1
08.59	2	908.7
07.58	2	922.4	10,9	4,6
06.96	3	930.8	8,6	1,4
05.51	4	950.6	6,3	-1,0
03.27	5	981.2	9,7	4,6
2702.18	3	36996.2	7,4	-0,6
00.01	3	37025.9	5,1	-1,8
			10,8	2,2

Ultra-violet Band Systems of the Mercury Iodide Molecule 327

TABLE 2 (contd.)

Wavelength	Int.	Wave number	Classification (ν, ν'')	Obs-cal.
2697.91	2	954.8	8,5	13.8
96.93	2	068.2	6,2	-2.5
96.65	2	072.0	11,9	1.3
95.80	2	083.8
95.51	1	087.8	9,6	0.9
94.34	2	103.8
93.74	2	112.1	7,3	-1.6
92.72	3	126.2
92.24	3	132.8	10,7	1.0
91.27	2	146.2	5,0	-5.0
91.00	3	149.9
90.19	2	161.1	8,4	4.5
89.81	2	166.3	13,11	1.7
88.87	2	179.3	11,8	2.7
88.07	2	190.4	6,1	-0.6
87.64	3	196.3
87.37	4	200.9	9,5	1.5
86.73	3	208.9	14,12	-2.5
86.07	2	218.1	12,9	-3.3
85.07	3	232.0	7,2	-0.8
84.35	2	242.0
83.93	2	247.7
83.21	2	257.7	15,13	-0.4
82.62	3	266.0	13,10	-1.1
81.69	2	278.9	8,3	5.4
81.21	2	285.6	11,7	0.9
80.73	2	292.2
79.22	2	313.3	14,11	2.6
			9,4	-0.8
78.63	3	321.4
78.27	3	326.4	12,8	-0.9
2677.29	3	37340.1
76.81	3	346.8
76.33	2	353.5	10,5 } 15,12 }	-1.1 } -1.7 }
75.26	4	368.4
74.95	3	372.8
74.16	1	383.8
73.52	3	392.8	8,2 } 11,6 }	0.2 } 2.2 }
72.72	2	403.9	16,13	4.3
71.72	2	418.0	14,10	4.8
71.42	3	422.2
71.00	3	428.1
70.53	2	434.6	9,3 } 12,7 }	3.6 } -0.6 }
70.03	1	441.6	17,14	-2.4
69.57	2	448.1
69.24	3	452.7	15,11	-1.8
68.58	2	462.0	10,4	-7.3
67.80	1	472.9	13,8	-2.8
67.23	2	480.9	7,0	3.5
66.52	2	491.0	16,12	-5.7
65.81	2	500.9	11,5	-6.6
64.82	3	514.8	14,9 } 8,1 }	-1.1 } 1.4 }
63.64	4	531.5
63.19	0	537.8	12,6	-7.4
62.48	4	547.8	9,2	-2.3
61.30	5	564.4	15,10	-2.6
60.76	4	572.1
60.07	3	581.8

TABLE 2 (contd.)

Wavelength	Int.	Wave number	Classification (v', v'')	Obs-cal.
59.36	3	591.8	16,11	-4.2
58.78	2	600.1
58.12	2	609.4
57.66	2	615.9	11,4	-6.3
57.56	3	617.3	14,8	-4.5
56.68	2	629.8	17,12	-6.2
2654.84	2	37655.9	12,5	-2.3
54.37	0	662.5	15,9	2.8
54.00	1	667.8
53.10	3	680.5
52.83	2	684.4	13,6	-9.7
51.46	2	703.9	16,10	5.4
50.93	2	711.4
50.07	0	723.6	14,7	-6.3
49.59	0	730.4	17,11	-4.9
48.48	0	746.4	11,3	7.3
47.42	2	761.4	15,8	-4.2

TABLE 3

Intensity distribution in Hg I bands (System D)

$\begin{matrix} v'' \\ \swarrow \\ v' \end{matrix}$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	$\Delta G'$ ($v+\frac{1}{2}$)
0	2	3	5	5	2	3										175.0
1	5	4	2		3	2										172.8
2	5	2		2	3			2								172.3
3	5		2	2	1			3								167.6
4	5	3	2		3	3	2		3	2						164.7
5	2	3	1		4	2	1						1			165.5
6		2	2													162.8
7	2		3		3	3										165.8
8		3	3	2	2	2	3	4								153.5
9			3	2	2	4	1	5	3							153.3
10			2	3	2	2	2	3	3	2						151.8
11				0	2	2	2	2	2	2						148.4
12						2	2	3	2	2						147.7
13							2	3	1	4	3	2				144.0
14								0	3	3	2	2	3			144.7
15									2	0	5	3	2	2		140.6
16											2	3	2	2		138.7
17												0	2		1	
$\Delta G''$ ($v+\frac{1}{2}$)	123.2	121.6	116.3	120.3	112.6	112.6	105.6	107.5	104.2	99.1	107.1	101.3	91.5			

The values of ΔG shown in this table cannot be considered as very satisfactory, the irregularities are very probably due to the diffuseness of the bands and consequent uncertainties in the determination of their wave lengths.

Tables 4 and 5 give the measurements, classification and the intensity distribution among the bands of system C. About 86 bands have been obtained, some of them being new. The ΔG values of the lower state of this system accord

Ultra-violet Band Systems of the Mercury Iodide Molecule 329

fairly closely with the corresponding values shown in Table 3 for system D. That these two systems have a common final state is indicated by the following formula calculated for system C

$$\nu = 32730.9 + [235.6(v' + \frac{1}{2}) - 2.16(v' + \frac{1}{2})^2] - [125.9(v'' + \frac{1}{2}) - 1.07(v'' + \frac{1}{2})^2]$$

TABLE 4
Mercury iodide bands (system C)

Wave-number (Wieland)	Int	Wave-number (Authors)	Int	Classification	Obs-cal.
32536.2	4	32540.3	5	0,2	0.9
650.0	4	650.3	3	2,5	4.7
		652.3	5	1,3	2.1
660.0	5	661.1	4	0,1	0
761.3	4	763.1	4	2,4	2.3
770.9	3	772.1	4	1,2	2.4
782.8	5	784.9	4	0,0	0
870.1	4	872.8	5	2,3	-5.4
		891.6	4	1,1	2.3
974.7	1	976.6	3	4,6	1.1
		988.1	3		
997.0	2	999.6	4	2,2	1.9
33014.4	3	33017.2	5	1,0	2.0
		021.5	5		
		33085.3	1	4,5	-1.3
		097.2	1		
33102.4	1	103.4	3	3,3	0.6
118.9	1	120.0	3	2,1	0.6
188.7	1	190.9	1	5,6	7.4
199.7	2	204.8	1	4,4	3.0
		222.3	2	3,2	2.0
242.8	4	243.3	5	2,0	0.1
		293.1	2	5,5	-3.5
319.8	1	319.9	3	4,3	0.7
341.4	5	342.2	5	3,1	0.2
		358.3	2		
		390.1	2	6,6	-7.1
414.3	2	416.1	4	5,4	4.3
437.3	3	438.6	4	4,2	-2.1
464.8	3	466.5	4		
		479.4	1		
		494.5	1	7,7	4.9
506.8	3	510.2	3	6,5	-0.1
		520.6	3		
531.0	2	530.6	2	5,3	1.4
558.5	4	559.1	5	4,1	-1.8
589.0	1	589.0	5	8,8	5.2
		631.0	2	6,4	5.5
650.6	4	649.2	4	5,2	0.5
		652.5	4		
680.1	1			4,0	2.6
711.3	1	739.8	4	8,7	-3.8
739.2	2	739.8	3	6,3	-3.0
771.7	3	771.2	3	5,1	0.8
803.1	2	803.1	2	8,6	-0.5
		810.5	2		
827.1	1	831.5	2	7,4	2.6
858.6	3	859.4	3	6,2	-3.0
862.0	3				

TABLE 4 (contd.)

Wave-number (Wieland)	Int.	Wave number (Authors)	Int.	Classification	Obs-cal.
33891.9	1	33892.7	3	5,0 }	-1.5 }
...	9.7 }	3.4 }
944.2	2	909.6	2	8,5	-7.1
949.4	2	946.1	4	7,3	-0.2
977.7	1	950.6	3	11,10	1.3
982.9	2	978.2	3	6,1	-5.9
34028.0	3
061.6	1	34030.7	4	8,4	-1.2
...	...	065.0	2	7,2	-0.8
110.4	1	084.1	2	10,7	2.3
...	...	110.7	5	6,0 }	2.8 }
143.6	3	9,5 }	-2.7 }
186.8	1	144.6	4	8,3	-2.7
223.1	3	181.9	2	7,1	0.4
226.0	4
...	...	226.2	4	9,4	-2.4
304.1	3	263.3	3	8,2	-5.5
337.2	2	300.8	4	10,5	-5.1
...	...	338.9	3	11,6 }	1.6 }
381.4	2	9,3 }	-7.1 }
408.6	0	382.5	3	8,1	-8.0
415.1	1
...	...	417.0	3
451.3	0	423.2	2	10,4	2.1
457.8	2
...	...	460.3	3	9,2 }	-5.2 }
489.9	2	12,7 }	6.6 }
512.6	1	492.7	2	11,5	-1.3
534.6	0	512.1	3
566.2	0	538.9	3	10,3	-0.4
...	...	567.8	3	12,6	3.0
611.1	0	593.6	2	14,9	0.4
642.9	2	614.1	4	11,4	4.9
676.5	0	640.8	3	13,7	7.7
715.1	2	677.6	3	12,5	-0.8
...	...	716.8	3
34750.7	2	726.0	2	16,11	2.2
...	...	34753.1	2	13,6	9.0
786.9	0	764.8	1	15,9	1.2
...	...	789.0	3	12,4	0.4
821.5	2	806.6	4	14,7	-2.1
860.3	0	821.0	3	16,10	-5.2
890.8	1	868.3	0	15,8	-2.5
893.8	2
931.6	2
964.6	0	928.9	3	16,9	-1.8
35000.1	0	965.0	0
...	...	35005.0	0
...	...	35040.6	2	16,8	3.2

Isotope Effect.—As iodine has no isotopes, the band spectra of iodides are particularly suitable for the study of the isotopes of the combining atom—Hg in this case. The known isotopes of Hg and their percentage abundance are given below (Seaborg, 1944).

196, 198, 199, 200, 201, 202, 204

0.15, 10.1, 17.0, 23.3, 13.2, 29.6, 6.7

Ultra-violet Band Systems of the Mercury Iodide Molecule. 331

TABLE 5
Intensity Distribution (System C)

v'/v''	0	1	2	3	4	5	6	7	8	9	10	11	ΔG ($v+\frac{1}{2}$)
0	4	4	5										231.5
1	5	4	4	5									225.6
2	4	3	4	5	4	3							224.4
3	4	5	2	3	3	5							216.9
4	3	5	4	3	1	1							210.2
5	5	3	4	2	4	2							209.3
6		3	3	3	2	3							204.0
7		2	4	4	2			1					198.2
8		3	3	4	4	2		4	5				198.4
9			3	3	4	5		3					193.1
10				3	3	4		2					197.0
11					4	2							176.5
12					3	3		3					182.9
13								3					165.8
14								4		2			171.2
15									0	1			168.2
16									2	3	3	2	
$\Delta G''$ ($v+\frac{1}{2}$)	125.8	119.8	120.2	114.1	117.3	111.5	110.2	99.8	108.2	107.9	95.0		

The separation of the isotopic heads of a given band (v' , v'') is given by

$$v' - v'' = (P - 1) [(v - v_e) - \chi'\omega' (v' + \frac{1}{2})^2 + \chi''\omega'' (v'' + \frac{1}{2})^2]$$

Where v' refers to the less abundant molecule. The isotopic separation is calculated from this formula for the two isotopes 198 and 202. The maximum separation is about 5 to 6 units and is certainly measurable for the bands remote from the origin. Examination of the spectrum failed to reveal any faint heads which could unmistakably be assigned as such. They must have been marked by the considerable overlapping arising from the unresolved rotational structure and the proximity of bands due to different vibrational transitions. The diffuseness of the bands justifies this assumption.

INTERPRETATION

The ultra violet emission spectra of mercury fluoride was analysed by Howell (1943) into two systems which were interpreted as the two components of a $^2\Pi - ^2\Sigma$ transition with the $^2\Pi$ interval Δv being 3940 cm^{-1} . By a comparison of this separation with the over all width of the 3P state of the Hg atom, Howell showed that the molecular constant $\Lambda (= \Delta v)$ for a Π electron giving rise to a $^2\Pi$ state in HgF is of the same order as the coupling constant $a (= 2265)$ for the $6p$ electron giving the $6s 6p^3P$ state of the Hg atom. This approximate equality together with the important observation by Carnell that all the ultra violet band spectra of the halides of Zn, Cd and Hg studied by him occur near the resonance lines of the metal atom led Howell to put forward the view that the transition involved in the emission

of the band systems of these halides is atomic in nature. The doublet splitting of the ${}^2\Pi$ state should then be nearly the same in all the halide bands of any particular metal atom Zn, Cd or Hg, the influence of the halogen atom being negligible. This feature was shown by Howell to hold in the various halide bands for which data were available. Examining the HgI band systems C and D in the light of this view, it would appear that these systems might form the two components ${}^2\Pi - {}^2\Sigma$ transition, the interval ${}^2\Pi_{3/2} - {}^2\Pi_{1/2}$ being equal to 3538 cm^{-1} . In Table 6, the separations between the (0,0) bands of what are believed to be such analogous components in the halides bands of Zn, Cd and Hg are collected. The data are mostly tentatively suggested by Howell (*loc. cit.*). The value for Hg Cl is confirmed recently by one of the authors (Rao, 1944), and that for HgI is from the present work.

TABLE 6

	Hg	Zn	Cd
F	3934	1179	370
Cl	3889	1115	383.5
Br	—	—	408
I	3510	—	—
Atomic coupling constant	4265	1140	386

There is a definite decrease in the value of the molecular constant from the lightest Hg F to the heaviest Hg I molecule, indicating an increasing departure from the atomic coupling constant 4265 cm^{-1} , a feature which should be expected as the influence of the halogen atom, cannot be altogether neglected. Accurate data on the other spectra are also needed before further light can be thrown on this question. Experiments in this direction are in progress in this laboratory.

ANDHRA UNIVERSITY,
GUNTUR

REFERENCES

- Howell, 1943, *Proc. Roy. Soc. (Lond.) A*, **182**, 95.
 Pritheshejewa, 1932, *Phys. Z. Sowjet.* **1**, 189.
 Rao K. R., 1944, *Curr. Sci.* **23**, 279.
 Sastry, 1942, *Proc. Nat. Inst. Sci. India*, **8**, 289.
 Seaberg, 1944, *Rev. Mod. Phys.*, **15**, 1.
 Wieland, 1929, *Helv. Phys. Acta*, **2**, 46 and 77.
 Wieland, 1932, *Zetts. f. Phys.*, **76**, 801