ULTRAVIOLET BAND SYSTEMS OF THE MERCURY IODIDE MOLECULE. PART III

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(Plate V)

ABSTRACT. The band spectrum of the mercury iodide molecule has been investigated further in the ultra-violet in the region between λ 2400 – 2000,λ as excited by a specially constructed high frequency oscillator. The G and H systems are considerably extended ; the G-system is analysed for the first time and a new vibrational scheme is suggested for the H-system, different from that proposed by Prihesheejewa   The vibrational constants are

G-system	... 88.4	0.2	125.7	1.2
H-system	... 97.1	1 05	125.3	1.15
	w_e'	$x_e'w_e'$	w_e''	$x_e''w_o''$

The two systems have a common final level which is the same as that for the C and D systems. In the H-system, the progressions are abruptly cut off after $v'=2$; this is considered as an instance of predissociation not found in any of the systems of the mercury halides so far analysed.

INTRODUCTION

The emission spectrum of the mercury iodide molecule was found to consist of seven band systems in the region λλ 4400 –2100 as listed by Rao, Sastry and Krishnamurty (1944) in Part I of these papers which contains a review of the work done by previous investigators on these bands. The systems were designated as B, C, D, E, F, G, and H in the order of decreasing wavelength, the H system occurring at the most refrangible end of the spectrum. Three more systems, were later discovered by Ramkrishna Rao and K. R. Rao (1946) and described in Part II ; they lie in the region between the F and G systems and hence designated as F_1, F_2 and F_3. The systems B, C, D, and E are extensive, each consisting of quite a large number of bands, while the others extend over shorter regions and are somewhat fragmentary. Vibrational analysis was suggested only for C and D and F_1 and F_3, all of which were shown to have a common lower state, probably the ground state of the molecule with the approximate vibrational constants $w_e' = 125.2$ and $x_e w_e' = 1.1$. It was shown further that the two systems C and D whose (0,0) bands have a wavenumber separation of 3510 cm^{-1} might form the components of the electronic transition $\pi^2 \longrightarrow \Sigma^2$, analogous to similar systems established by Howell (1943) in the HgF bands and by Rao and Ramchandra Rao (1944) in the HgCl bands.

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With a view to the elucidation of the entire band system of the Hg I molecule, further work is carried out and in this part, the results relating to the G and H systems will be described. When the structure of the entire band systems is completely known, it would be of interest to examine why many systems are emitted by this molecule while only a few are known to exist in each of the corresponding molecules HgF, HgCl and HgBr, as well as in the halides of the other elements, zinc and cadmium of the same periodic group. It is hoped that some of the ten characteristic systems of Hg I might prove to be intercombination bands due to transitions between excited states of the molecule.

<center>E X P E R I M E N T A L</center>

A pure sample of mercury iodide is taken in a thin-walled pyrex tube about 8″ long and half-inch internal diameter. The tube is continuously evacuated by a Cenco Hyvac pump and excited by a radio frequency voltage, available at the ends of the tank circuit of a Hartley shunt-fed valve oscillator of 1 to 10 Mega cycles range. The heat of the discharge is sufficient to vaporise the mercury iodide in the tube. Within a minute of switching on the oscillator, the colour of the discharge turns intense blue, characteristic of the Hg I vapour. The spectrum is photographed by a Hilger Quartz E 315 spectrograph, using an exceedingly narrow slit. This narrow width has proved to be worthwhile in resolving some close band heads, in spite of their general diffused nature. Ilford Special Rapid plates sensitised by high grade mobil oil served well to photograph the spectrum below $\lambda2300$. Zenith 'Fast Ultra-Violet' plates of high speed and Ilford plates type Q III are also employed. Exposures of even two hours duration gave very good spectra. The copper arc standards are adopted for reducing the plates.

As pointed out in Part II, in view of the peculiarly large number of systems attributed to Hg I molecule, special care is taken to establish first, as far as possible, from an experimental standpoint the origin of these band systems and to examine that they are not due to other molecules or to the products of dissociation of mercury iodide. Comparison is made with spectra obtained under identical experimental conditions of various other halides and chifley iodides. The band spectra of the two molecules, mercury and iodine, have also been studied in detail in this respect. There is evidence on the plates of bands attributable to Hg_2 and Hg_3 but they occur in regions remote from that of G and H systems. As iodine is known to have an extensive band system observed in absorption and in emission below λ 3500 down to the vacuum ultraviolet, plates have been taken with iodine alone in the discharge tube and the data are compared with the bands ascribed to iodine by the previous investigators, Curtis and Evans (1933), Warren (1935), Venkateswarlu (1946). It is found that under the conditions adopted in our experiments no trace of iodine emission bands appeared in the region where the G and H systems of HgI occur. On the other hand, a general continuous spectrum is obtained extending down

a

b
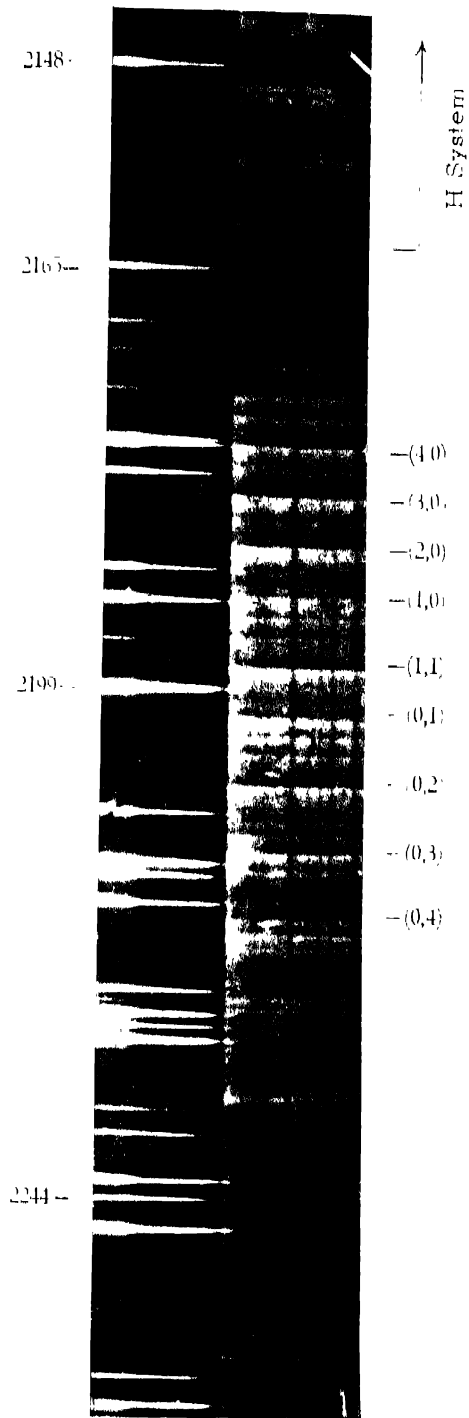
(*a*) G System with Culture.   (*b*) H System Comparison.
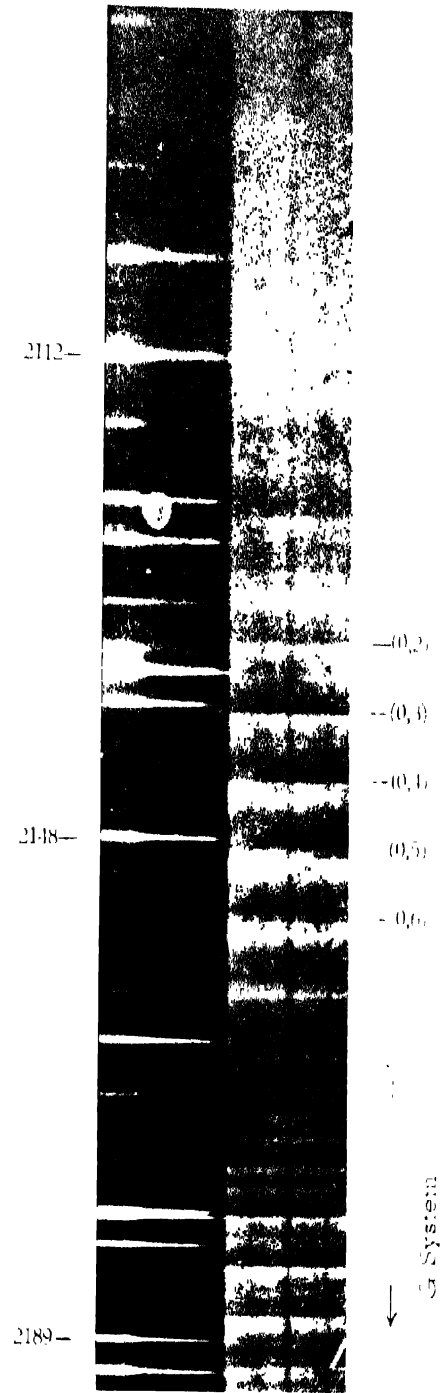
to λ 2000. It might be mentioned here that this iodine H. F. discharge could as well be employed as a source of continuous spectrum in the ultra-violet absorption experiments in place of the usual hydrogen discharge tube. Such a source has, in fact, proved very easy to set up and convenient to work with and is being employed in our laboratory with success. A full description of this will be found elsewhere. The above experiments have led the authors to consider the mercury iodide molecule as the emitter of the G and H systems. A further confirmation is afforded by the vibrational analysis of the two systems suggested in the succeeding sections.

<center>R E S U L T S</center>

G System.—This system, lying between λλ 2230—2165, was first reported by Prilheshejewa (1932) who published measurements of 22 band heads which were from a low dispersion spectrogram in which the individual members of the sequences could not obviously have been sufficiently resolved. Even the direction of degradation of the bands was not definitely observed. No analysis or regularities were suggested by him. In the present work the dispersion used is about 5 A. U. per mm. in this region ; a much larger number of band heads, about fifty in all, are measured. They are found to be clearly red-degraded with sharp heads towards the violet side. A reproduction of this system is given in Plate IV which is a four-hour exposure with copper arc comparison.

The wave-lengths, intensities and wave-numbers of the band heads are given in Table I. The intensities are visual estimates. For comparison, the data reported by Prilheshejewa are also given in the first column. The analysis of the system is found to be comparatively easy as the heads are characteristically prominent and fairly resolved.

<center>TABLE I</center>

<center>Band heads of the G-System.</center>

Wave length		Int.	Wave number	Classifica-tion
Prilheshejewa	Authors			
2239.7				
2234.60	2234.30	0	44742.7	(4,10)
	2233.50	1	44758.7	(3,9)
	2232.60	1	44776.7	(2,8)
	2231.61	3	44796.7	(1,7)
	2229.22	0	44844.8	(4,9)
	2228.22	1	44864.9	(3,8)
2227.2	2227.37	2	44882.0	(2,7)
	2226.29	3	44903.7	(1,6)
	2225.21	0	44925.6	(0,5)
	2223.06	0	44969.0	(3,7)
	2221.88	2	44992.9	(2,6)

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TABLE I (contd.)

Band heads of the G-system.

Wave length		Int.	Wave number	Classifica-tion
Prilheshejewa	Authors			
2220.5	2220.74	4	45016.0	(1,5)
	2219.38	3	45043.6	(0,4)
	2218.71	0	45057.2	——
	2215.02	4	45132.2	(1,4)
2213.2	2213.61	5	45161.0	(0,3)
	2212.08	2	45192.2	(3,5)
	2211.17	1	45210.8	(2,4)
	2210.86	0	45219.6	——
	2209 12	1	45252.7	(1,3)
2208.0	2207.78	6	45280.2	(0,2)
	2207.03	0	45295.6	(3,4)
2205.0	2205.12	3	45334.8	(2,3)
2204.6	2203.63	4	45365.5	(1,2)
	2202.56	0	45387.5	(4,4)
2202.4	2201.92	4	45400.7	(0,1)
	2201.00	2	45419.7	(3,3)
	2199.59	2	45448.7	(2,2)
2196.0	2197.67	6	45488.4	(1,1)
	2196.24	0	45518.1	——
	2195.12	4	45541.3	(3,2)
2193.3	2193.53	4	45574.3	(2,1)
	2192.50	3	45595.7	(5,3)
2191.5	2191.72	4	45611 9	(1,0)
2190.0	2190.94	2	45628.1	(4,2)
	2189.67	1	45654.6	(3,1)
	2188.45	3	45680.1	(6,3)
2188.2	2187.55	6	45698.8	(2,0)
	2187.01	0	45710.1	(5,2)
2185.3	2185.63	1	45739.1	(4,1)
	2184.23	0	45768.4	(7,3)
2183.5	2183 36	5	45786.5	(3,0)
	2181.02	3	45835.7	(5,1)
2180.7	2179.33	5	45871.3	(4,0)
	2178.64	0	45885.7	(7,2)
	2176.80	3	45924.6	(6,1)
2175.0	2175.13	4	45959.8	(5,0)
	2174.44	1	45974.3	(8,2)
	2173.75	1	45988.9	——
	2172.69	3	46011.4	(7,1)
2171 4	2171.06	2	46046.9	(6,0)
	2170.49	1	46058.1	(9,2)
	2169.68	0	46075.2	——
2168.5	2168.76	1	46094.8	(8,1)
2168.0	2168.05	0	46109.8	——
	2167.16	0	46128.8	(7,0)
	2166.60	00	46140.7	——
	2165.99	0	46153 7	—

TABLE II

Vibrational analysis of G-system HgI.

$v''\backslash v'$	0	1	2	3	4	5	6	7	8	9	10	
0	45611.9(4)	45400.7(4)	45280.2(6)	45161.0(5)	45043.6(3)	44925.6(0)	44905.7(3)	44796.7(3)	44776.7(1)	44758.7(1)	44742.7(0)	125.1
1	45698.8(6)	45488.4(6)	45365.5(4)	45252.7(1)	45132.2(4)	45016.0(4)	44992.3(2)	44882.0(2)	44864.9(1)	44844.8(0)		120.6
2	45786.5(5)	45574.3(4)	45448.7(2)	45334.8(3)	46210.8(1)			44969.0(0)				116.5
3	45871.3(5)	45654.6(1)	45541.3(4)	45419.7(2)	45295.6(0)	45192.2(2?)						121.5
4	45950.8(4)	45739.1(1)	45628.1(2)		45387.5(0)							112.5
5	46046.9(2)	45835.7(3)	45710.1(0)	45595.7(3)								112.3
6	46128.8(0)	45924.6(3)		45680.1(3)								108.7
7		46011.4(3)	45885.7(0)	65768.4(0)								104.7
8		46094.8(1)	45974.3(1)									106.2
9			46058.1(1)									102.2
	87.7	84.4	86.3	86.6	89.9	86.8	85.7	86.5	83.8			

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TABLE III

v'' / v'	0	1	2	3
0	46625	46499	46382	46262
1	46846	46724		
2	47058	46930		
3	47262	47136		

Table II presents the bands in the usual diagonal array. It will be seen that most of the intense bands fall into the v' progression with $v''=0$ and v'' progressions with $v'=0$ and 1; the intensity distribution is such that the Frank-Condon parabola is very wide and open, the (o, o) band being absent. The $x'_e w'_e$ values are not, in spite of the sharpness of the band heads, very regular; but the general scheme is believed to be correct. The following vibrational formula is calculated for the bands by plotting the $\Delta G(v)$ values against the quantum numbers and adopting the graphical method.

$$\nu = 45542.4 + (88.4\ u'-0.2u'^2)-(125.7\ u''-1.2u''^2) \text{ where } u'=(v'+\tfrac{1}{2}) \text{ etc.}$$

The values 125.7 and 1.2 indicate that the lower state of this system is the same as that determined previously for the C and D systems.

H-System.—This system too was first reported by Prilheshejewa but the number of bands was only ten. The scheme in Table III was also tentatively suggested by the above author, which, according to the present work, appears to be very fragmentary and uncertain. Several bands reported as single by Prilheshejewa are observed to consist of blends of two or more heads and hence an altogether different vibrational analysis has been obtained. The new scheme is presented in Table IV and Table V gives the details of the measurements. Twenty-two band heads are measured between $\lambda\lambda$ 2170-2110. The degradation of the bands, as can be seen from the reproduction, Plate IV is definitely towards the red as in the G-System. This feature suggested the rearrangement of the heads shown in Table IV, which leads to a value of $w_e' < w_e''$, while the Prilheshejewa's scheme gives $w_e' > w_e''$ unusual for red-degraded bands. Further, if Prilheshejewa's analysis is adoped, many of the strong bands would be left out of the scheme. With our analysis all the bands can be represented by the formula,

$$\nu = 47110.2 + (97.1\ u'-1.65u'^2)-(125.3\ u''-1.15\ u''^2)$$

The $\Delta G(v'')$ values for this system are much more regular than those for the G-system and the constants calculated for the lower state are considered as accurate. For the upper state the constants are derived from only two $\Delta G(v')$ values.

TABLE IV

Vibrational analysis of H-system HgI.

v'' / v'	0	1	2	3	4	5	6	7	8	9
0	47188.0(0)122.7	46972.7(1)112(0 c	46852.7(5)117.2	46735.5(6)115.7	46619.8(5)114.4	46505.4(3)112.7	46393.2(1)			
93.5		92.6	92.6		92.9	95.6	94.5			
1		47065.3(2)	46945.3(2)		46(12.7(0)111.7	46501.0(4)115.3	46481.7(5)105.5	463.78 9(3)107.1	45271.8(1)	
92.5		89.5			89.7			9.06	9.15	
2		47154.8(1)			46802.4(1)			46469.5(4)106.5	46363.3(4)106.2	46257.1(3)
	112.7	120.0	117.2	115.7	113.1	112.7	108.8	166.6	166.2	

TABLE V

Band heads of the H-system.

Wave length	Int.	Wave Number		Classifica-tion
		Authors	Prilhesliejewa	
2161.15	3	46257.1	46262	(3,9)
2160.46	2	46271.8		(1,8)
2156.20	4	46363.3		(2,8)
2155.48	3	46378.9	46382	(1,7)
2154.81	1	46393.2		(0,6)
2151.27	4	46469 5		(2,7)
2150.43	5	46487.7		(1,6)
2149.61	3	46505.4	46499	(0,5)
2145.20	4	46601.0		(1,5)
2144.33	5	46619.8	46625	(0,4)
2141.35	oo	46684.8		(2,5)
2140.07	o	46712.7		(1,4)
2139.02	6	46735.5	46726	(0,3)
2135.96	1	46802.4		(2,4)
2134.62	oo	46832.0		(1,3)
2133.67	5	46852.7	46846	(0,2)
2129.46	2	46945.3	46930	(1,2)
2128.22	3	46972.7		(0,1)
2124.03⁻	2	47065.3	47058	(1,1)
2120.00	1	47154.8	47136	(2,1)
2118.51	o	47188.0		(1,0)
2114.82	oo	47270.2	47262	(2,0)

The intensities of the bands present interesting peculiarities. Fig. 1 shows the potential curves drawn to scale, for the upper and lower states of this system and the transitions taking place according to Frank-Condon principle. The parabola of intensities thus obtained is indicated by a continuous line on the right side of the figure, inset in the small table giving the observed intensity distribution among the bands. It is a very wide and open one with the vertex shifted towards higher v'' values, the (0, 3) and (0, 4) bands being the most intense of the entire systems.

Another feature of this system is the existence of only three v'' progressions after which there is an abrupt termination of the bands; there is no band with $v' > 2$. This is considered to be an instance of predissociation, not found in any of the other systems of HgI so far analysed. The phenomenon of predissociation first observed in the S_2 bands has since been noted in band systems of several other molecules (cf. Jevons 'Report' 1932). In S_2, two points of predissociation were observed and abrupt changes in the appearance of the bands occur at these points; further, the bands which have diffuse structure in
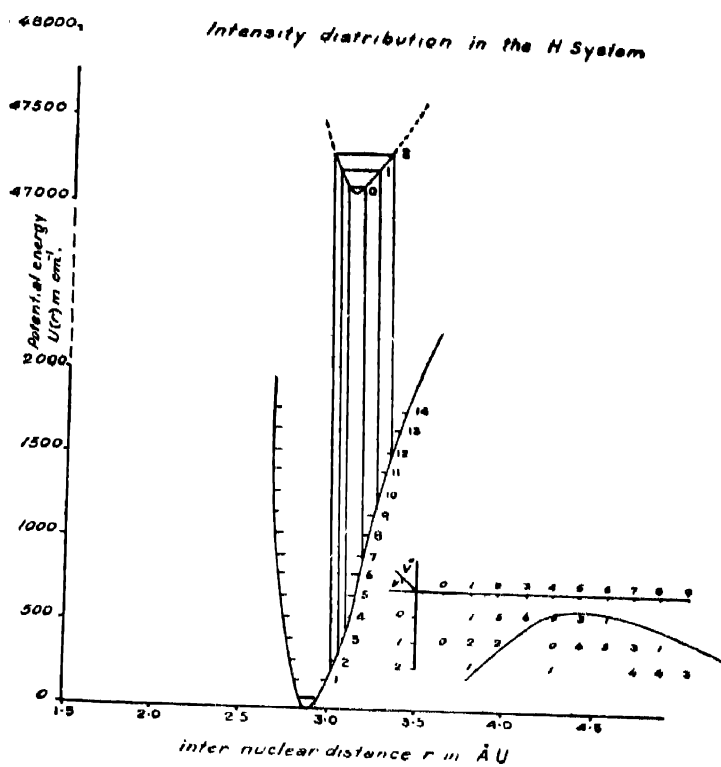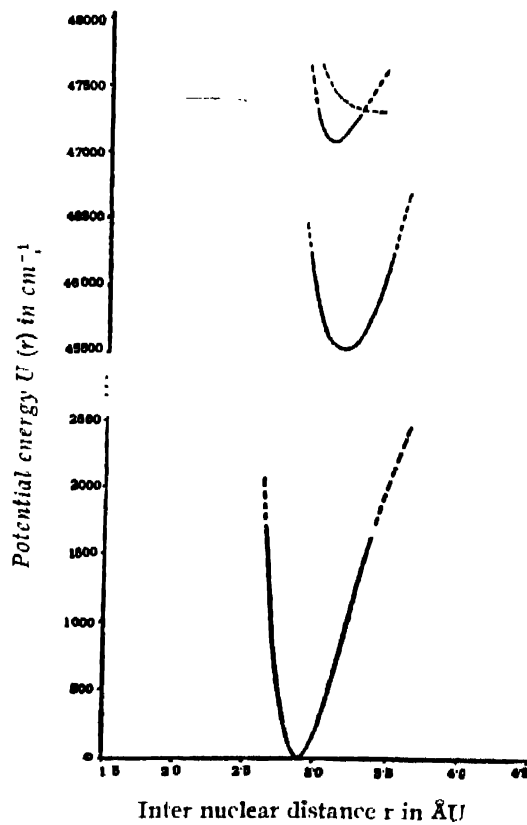
48000

Intensity distribution in the H System

47500

47000

Potential energy U(r) in cm⁻¹.

2000

1500

1000

500

0

1·5   2·0   2·5   3·0   3·5   4·0   4·5

inter nuclear distance r in ÅU

FIG. 1

48000

47500

47000

46500

46000

45500

Potential energy U (r) in cm⁻¹,

2500

2000

1500

1000

500

0

1·5   2·0   2·5   3·0   3·5   4·0   4·5

Inter nuclear distance r in ÅU

FIG. 2

absorption do not at all occur in emission. Similarly in the β system of nitric oxide, bands with $v'>4$ are observable in absorption but not in emission. In yet other bands, such as the v'' progression of the N_2 second positive system a sudden cut off occurs in emission and the systems do not occur even in absorption. All these characteristics have been interpreted as due to the interaction of the upper state with an unstable electronic state of the molecule giving rise to radiationless transitions. The repulsive curve of such a possible electronic state, intersecting the curve for the upper state of the H-system is indicated in Fig. 2 which shows the potential energy curves for the G and H-systems of the HgI molecule.' A complete understanding of the nature of the predissociation is not yet possible unless the absorption of HgI in this region is also studied in detail. Experiments with a view to studying this particular feature are in progress and further discussion will be presented later.

The vibrational constants, the estimated value of the dissociation energy and E(atom) for the upper and lower states are given in Table VI. The values indicate a common lower state, same as that for the C and D systems. The nature of the upper electronic state is difficult to determine. Some of the bands of the G-system are accompanied by fainter sub-bands which cannot be of isotopic origin. They are probably P components if the upper electronic state of this system is a $^2\pi$. For the H-system, the upper state is probably a $^2\Sigma$.

.Table VI

System	w_e'	w_e''	D'	D''	E_atom	Dissociation products of the upper state,
G	88.4	125·7	1.21	0.44	6.48	$Hg(^1P) + I(^2P)$
H	97.1	125.3	0.16	0.44	5.63	$Hg(^2P) + I(^2P)$

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