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# ULTRA VIOLET BAND SYSTEMS OF THE MERCURY IODIDE MOLECULE—PART II

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(Plate VI)

**ABSTRACT**. Continuing the study of the bands of the mercury iodide molecule three new systems are obtained between λ 2530 and λ 2320 which are designated as $F_1$, $F_2$ and $F_3$ systems. Vibrational analysis is given for the $F_1$ and $F_3$ systems and regularities are presented among the bands of the $F_2$ system. $F_1$, $F_3$, C and D systems are found to have a common final state which is presumably the ground state of the HgI molecule.

## INTRODUCTION

In Part I of these investigations, Rao, Sastry and Krishnamurty (1944) showed that the band spectrum of the mercury iodide molecule consists of seven different systems (designated by them as B, C, D, E, F, G and H). Of these, analysis is known definitely only for the two systems C and D. These were shown to have a common ground state with vibrational constants $\omega''=125.8$ and $\chi''\omega''=1.09$ cms$^{-1}$, which are in keeping with the corresponding values for the other halides of mercury, as seen from Table I below.

TABLE I

| | $\omega''$ | $\chi''\omega''$ |
|---|---|---|
| HgF | 490.8 | 4.05 |
| HgCl | 293.4 | 1.82 |
| HgBr | 186.3 | 0.98 |
| HgI | 125.8 | 1.09 |

It was also suggested that the two systems form the components of an electronic transition $^2\Pi-{}^2\Sigma$ with the $^2\Pi$ interval 3538 cms$^{-1}$, being approximately equal to the atomic coupling constant for the 6p electron giving the 6s 6p $^3P$ state of the mercury atom. Further work on these band systems has been undertaken by the authors in order to interpret the remaining band systems. In the course of this attempt, new band systems have been observed which are considered as due the mercury iodide molecule. The purpose of this paper is to report the data and the analysis, as far as is obtained, of the new bands.† A consideration of the entire band systems will be taken up in another communication.

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## EXPERIMENTAL

The bands are excited, in an ordinary H-form pyrex discharge tube, by a transformer, as described previously in Part I. In addition to this source, the emission bands are obtained also by the use of a specially constructed valve oscillator of low power designed to give a frequency of one to five megacyles. The substance is heated in a quartz tube with an end-on sealed quartz window for observation and evacuated continuously by a Cenco Hyvac pump. The electrodes are external and the distance between them is varied. When the discharge is bright bluish violet, the mercury iodide bands are emitted intensely. Exposures of half an hour to six hours are given depending on the dispersion of the instrument used.

## RESULTS

Besides the seven previously known systems, three systems are newly obtained on our plates. They occur in the spectral region between the F and G systems and therefore designated as $F_1$, $F_2$, and $F_3$. They are shown in Plate VI.

The $F_1$ system consists of about twenty red-degraded bands, some of which have intense and sharp edges. The system extends over the short region $\lambda$ 2532 – 2455 just at the violet end of the F system, with which there may be a slight overlapping. The wave lengths of the bands and the wave numbers are shown in Table II. The large intensity of two of the bands $\lambda$ 2521 and $\lambda$ 2513 is probably due to the partial superposition by the strong and diffuse bands of the $Hg_2^+$ molecule at $\lambda$ 2525 and $\lambda$ 2518 which might also have obscured some of the weaker bands of the $F_1$ system.

The $F_2$ system consists of a succession of closely spaced bands degraded to the red with the interval between successive bands diminishing towards the longer wave lengths. About thirty bands of this system have been measured; several other fainter bands could be seen but not measured.

The $F_3$ system is small, comprising of about fifteen bands, diffuse in appearance but mostly headless. It resembles the brief system of mercury bromide reported by Rao and Ramachandra Rao (1944). As in the $F_1$ system there seems to be a partial overlapping of the bands at $\lambda$ 2341 and $\lambda$ 2337 by those of $Hg_2$ at $\lambda$2342 and $\lambda$2337. Tables III and IV present the band head data of systems $F_2$ and $F_3$ respectively.

As the bands constituting these three systems have not been recorded by any of the previous investigators, particular care was taken to establish by systematic experiments that they are not due to any possible impurity in the source or to other molecules containing mercury or iodine. Various spectra are taken and by comparison, the assignment of the systems to HgI is considered to have been confirmed from the experimental standpoint.

The vibrational scheme obtained for the $F_1$ system is shown in Table V in the usual diagonal array. A dozen bands have been included in the scheme, comprising nearly all the intense heads. Classification is not suggested

TABLE II—$F_1$ System

| Wave length. | Wave Number. | Intensity. | Classification. |
|---|---|---|---|
| 2532.83 | 39470.7 | 6 | 1,6 |
| 2530.08 | 39512 5 | 3 | 2,7 |
| 2528 50 | 39537.3 | 3 | 0,4 |
| 2526.21 | 39573.1 | 3 | 1,5 |
| 2523.37 | 39617.6 | (oo) | — |
| 2521.13 | 39652 8 | 7 | 0,3 |
| 2519 01 | 39686 9 | 3 | 1,4 |
| 2517.52 | 39709.7 | 3 | 2,5 |
| 2513.61 | 39771.4 | 8 | 0,2 |
| 2510 22 | 39825.3 | 4 | 2,4 |
| 2508 56 | 39851.5 | 2 | 3,5 |
| 2 06.28 | 39886.2 | 5 | 4,6 |
| 2500.87 | 39974.1 | 2 | 5,7 |
| 2487 97 | 40181.3 | 1 | — |
| 2485 94 | 40214 1 | 0 | — |
| 2476 76 | 40363.1 | (oo) | — |
| 2475.23 | 40387.1 | 0 | — |
| 2470.47 | 40465.9 | 0 | — |
| 2460.03 | 40638.6 | 0 | — |
| 2454.97 | 40721.5 | (oo) | — |

TABLE III $F_2$ System.

| Wave Length | Wave Number | Intensity | Classification |
|---|---|---|---|
| 2380.99 | 41986.3 | 0 | |
| 2381.15 | 41983.7 | 0 | |
| 2382.30 | 41963.4 | 1 | |
| 2385.13 | 41913.6 | 1 | |
| 2387.57 | 41870.3 | 1 | |
| 2388.77 | 41849 8 | 1 | |
| 2390.95 | 41816.2 | 1 | (5,v″) |
| 2393.94 | 41759.4 | 1 | (4,v″) |
| 2396.37 | 41717.1 | 1 | (3,v″) |
| 2397.40 | 41699.1 | 1 | (5,v″+1) |
| 2393.68 | 41677.9 | 0 | (2,v″) |
| 2400.51 | 41645.0 | 0 | (4,v″+1) |
| 2401.91 | 41620.9 | 2 | |
| 2403.42 | 41594.7 | 3 | (3,v″+1) |
| 2404.40 | 4 577.8 | 3 | (5,v″+2) |
| 2405.76 | 41554.3 | 3 | (2,v″+1) |
| 2406.71 | 41538.0 | 2 | |
| 2407 31 | 41527.3 | 3 | (4,v″+2) |
| 2408.29 | 41510.6 | 2 | |
| 2410.22 | 41477.4 | 4 | (3,v″+2) |
| 2412.63 | 41436.2 | 3 | (2,v″+2) |
| 2414.78 | 41399.1 | 4 | (1,v″+2) |
| 2416.74 | 41365.5 | 3 | (3,v″+3) |
| 2419.09 | 41325.3 | 4 | (2,v″+3) |
| 2421 12 | 41290.7 | 5 | (1,v″+3) |
| 2423 37 | 41252.3 | 3 | (0,v″+3) |
| 2424.81 | 41227.8 | 4 | (2,v″+4) |
| 2426 84 | 41193.3 | 2 | (1,v″+4) |
| 2428.83 | 41159.7 | 2 | (0,v″+4) |
| 2430 50 | 41131.3 | 2 | (2,v″+5) |
| 2432.50 | 41097 5 | 2 | (1,v″+5) |
| 2433 96 | 41072.8 | 2 | (0,v″+5) |
| 2435.85 | 41041.0 | 2 | (2,v″+6) |
| 2437.08 | 41020.2 | 2 | |

TABLE IV. $F_3$ SYSTEM

| Wave Length | Wave Number | Intensity | Classification |
|---|---|---|---|
| 2347.36 | 42587.3 | 00 | |
| 2346.35 | 42605.4 | 00 | 2,11 |
| 2345.49 | 42621.8 | 0 | 0,8 |
| 2344.51 | 42639.9 | 2 | 3,12 |
| 2342.56 | 42674.5 | 2 | 1,9 |
| 2340.92† | 42705.5 | 7bd | 2,10 |
| 2339.53 | 42731.1 | 1 | 0,7 |
| 2336.92† | 42778.6 | 5bd | 1,8 |
| 2335 64 | 42802,4 | 2 | 2,9 |
| 2334.68 | 42818.9 | 3 | 3,10 |
| 2333.60 | 42839.1 | 2 | 0,6 |
| 2332.23* | 42864.8 | 0 | |
| 2331.13 | 42885.0 | 2 | 1,7 |
| 2329.95 | 42905.3 | 4 | 2,8 |
| 2326.76± | 42964.3 | 6 | |
| 2321.97± | 43053.1 | 5 | |

*Probaly due to $Hg_2$ bands
†Superposed by $Hg_2$ bands
± Broad and complex

for eight weak bands towards the violet end ; they possibly represent heads involving higher ($v'$, $v''$) values. The analysis shows no bands with $v''=0$ or 1 ; the values of $\Delta G''(v)=118{\cdot}6$, 115,5, 114.7 etc., have suggested this particular vibrational numbering, beginning with $v''=2$. Such a feature might be expected in band systems characteristic of a molecule of the type of mercury iodide. A justification of the assignment is seen from the following formula calculated for the bands on the basis of this numbering :—

$$\nu=4000.5+[153.8(v'+\tfrac{1}{2})-2.0(v'+\tfrac{1}{2})^2]$$
$$-[124\ 5(v''+\tfrac{1}{2})-0.98(v''+\tfrac{1}{2})^2]$$

The constants for the final state $\omega''=124{\cdot}5$ and $\chi''\omega''=0.98$ agree closely with corresponding values for the C and D systems.

The structure of the $F_3$ system is shown in Table VI. Of the sixteen bands comprising this system all the strong ones with the exception of two have entered into the scheme. The overlapping by $Hg_2$ bands accounts probably for the abnormal intensity of the bands at $\lambda$2341 and $\lambda$ 2337 and for the divergencies in the $\Delta G''(v)$ involving these two bands, chiefly $\lambda$ 2341. The strong unclassified bands at $\lambda$ 2327 and $\lambda$ 2322 may be complexes of several close bands, which could not be resolved. $\lambda$ 2332 (0) may be due to $Hg_2$. As in the $F_1$ system, here too the $v''$ values assigned to the bands begin with higher values ; it is as high as $v''=6$. The following formula,

$$\nu=43521.5+[172.4(v'+\tfrac{1}{2})-10.5(v'+\tfrac{1}{2})^2]$$
$$-[124.6(v''+\tfrac{1}{2})-1.1(v''+\tfrac{1}{2})^2]$$

giving $\omega''=124.6$ and $\chi''\omega''=1.1$ is considered to be in support of the

TABLE V

Vibrational analysis of the $F_1$ system..

| $v''/v'$ | 2 | 3 | 4 | 5 | 6 | 7 | $\Delta G'(v)$ |
|---|---|---|---|---|---|---|---|
| 0 | 39771.4 (6) | 39652.8 (5) | 39437.3(1) | | | | 149.6 |
| 1 | | | 39686.9(1) | 39573.1(r) | 39470.7(4) | | 137.5 |
| 2 | | | 39825.3(2) | 39709.7(1) | | 39512.5(1) | 141.8 |
| 3 | | | | 39851.5(0) | | | |
| 4 | | | | | 39886.2(3) | | |
| 5 | | | | | | 39974.1(0) | |
| $\Delta G''(v)$ | 118.6 | 115.5 | 114.7 | 102.4 | | | |

TABLE VI

Vibrational analysis of the $F_3$ system.

| $v''/v'$ | 6 | 7 | 8 | 9 | 10 | 11 | 12 | $\Delta G'(v)$ |
|---|---|---|---|---|---|---|---|---|
| 0 | 42839.1(2) | 42731.1(1) | 42621.8(0) | | | | | 155.8 |
| 1 | | 42885.0(2) | 42778.6(5) | 4274.5(2) | | | | 127.3 |
| 2 | | | 42905.3(4) | 42802.4(0) | 42705.5(7) | 42605.5(00) | | 113.4 |
| 3 | | | | | 42818.9(3) | | 42639.9(2) | |
| $\Delta G(v'')$ | | 108.0 | 107 8 | 103.5 | 96.9 | 100.1 | | |

Table VII—Regularities in the band heads of the $F_2$ system

| $v''/v'$ | $v''$ | $v''+1$ | $v''+2$ | $v''+3$ | $v''+4$ | $v''+5$ | $v''+6$ | $\Delta G'(v)$ |
|---|---|---|---|---|---|---|---|---|
| 0 | | | | 41252 3(3) | 41159.7(2) | 41072.8(2) | | |
| 2 | | | 41399.1(4) | 41200 7(5) | 41193.3(2) | 41097.5(2) | | 32 2 |
| 2 | 41677 9(0) | 41554.3(3) | 41436.0(3) | 41225.3(4) | 41227 8(4) | 41131.3(2) | 41041 0(2) | 33.9 |
| 3 | 41717.1(1) | 41594.7(3) | 41477.4(4) | 41365.5(3) | | | | 40.3 |
| 4 | 41759.4(1) | 41645.0(0) | 41527 3(3) | | | | | 47 5 |
| 5 | 31816.2(1) | 41699.1(1) | 41577.8(0) | | | | | 53.8 |
| $\Delta G''(v)$ | 121.9 | 118.7 | 110.3 | 95.8 | 93.1 | 90.3 | | |

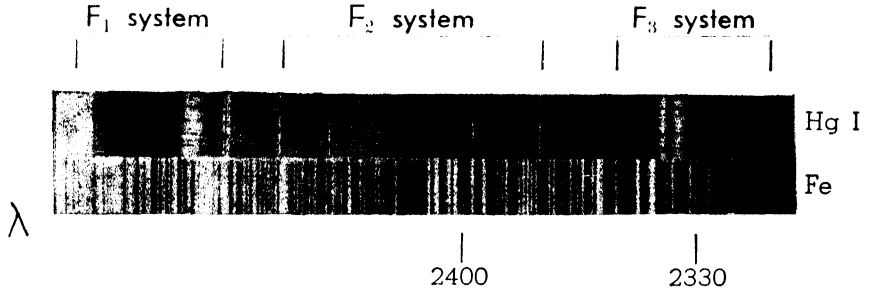


Fig. A. New Bands of the HgI molecule.

assignment. On the basis of this analysis the system $F_1$ and $F_3$ as well as C and D have a common final electronic state, which is presumably the ground $^2\Sigma$ state of the HgI molecule.

The $F_2$ system presents a different appearance altogether from the remaining bands, as can be seen from the reproduction of the bands in Plate VII. The authors have not succeeded in confidently arriving at a vibrational analysis of this system. Out of several attempts, the arrangement shown in Table (VII) may be pointed out. The order of the $\Delta G''(v)$ values agrees with the corresponding values for the classified system. But the second differences leading to $\chi''$ $\omega'$ are not consistent. The $\Delta G''(v)$ values are found to be increasing. The bands themselves have fairly sharp edges compared to the other system and large errors in measurement are not expected. The suggested $v',v''$ numbering must be treated as only tentative. No formula is therefore calculated for this system. Further work on this and the remaining systems is in progress and a discussion of all these will be presented in succeeding parts of the investigations.

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