# CHAPTER VII

## ELECTRON CONFIGURATION AND CONCLUSIONS

Our knowledge about a large number of electronic states obtained from their observed molecular spectra is complete only for a few diatomic molecules and for many molecules electronic states observed are not more than two or three. It is obvious that an understanding of the electronic states of molecules must be built upon a prior knowledge of the electronic states of their constituent atoms. Rules regarding the various types of molecular states which result from given states of participating atoms have been derived by Wigner and Witmer (1928) on the basis of quantum mechanics. These rules have been discussed in detail by Mulliken (1930, 1932) and Herzberg (1950).

The totality of the electronic states or what is usually known as the manifold of electronic states can be obtained by bringing together the component atoms of the molecules (building-up principle) or by splitting up of the hypothetical united atom; we are still lacking a criterion for the stability of these molecular states. However, mathematical methods have been developed to express the energy of a system of two atoms separated by a large distance (Heitler and London, 1927) and it is found possible to infer the nature of the variation of U(r) as the atoms approach making r smaller. This enables to determine whether a state will be repulsive or stable.

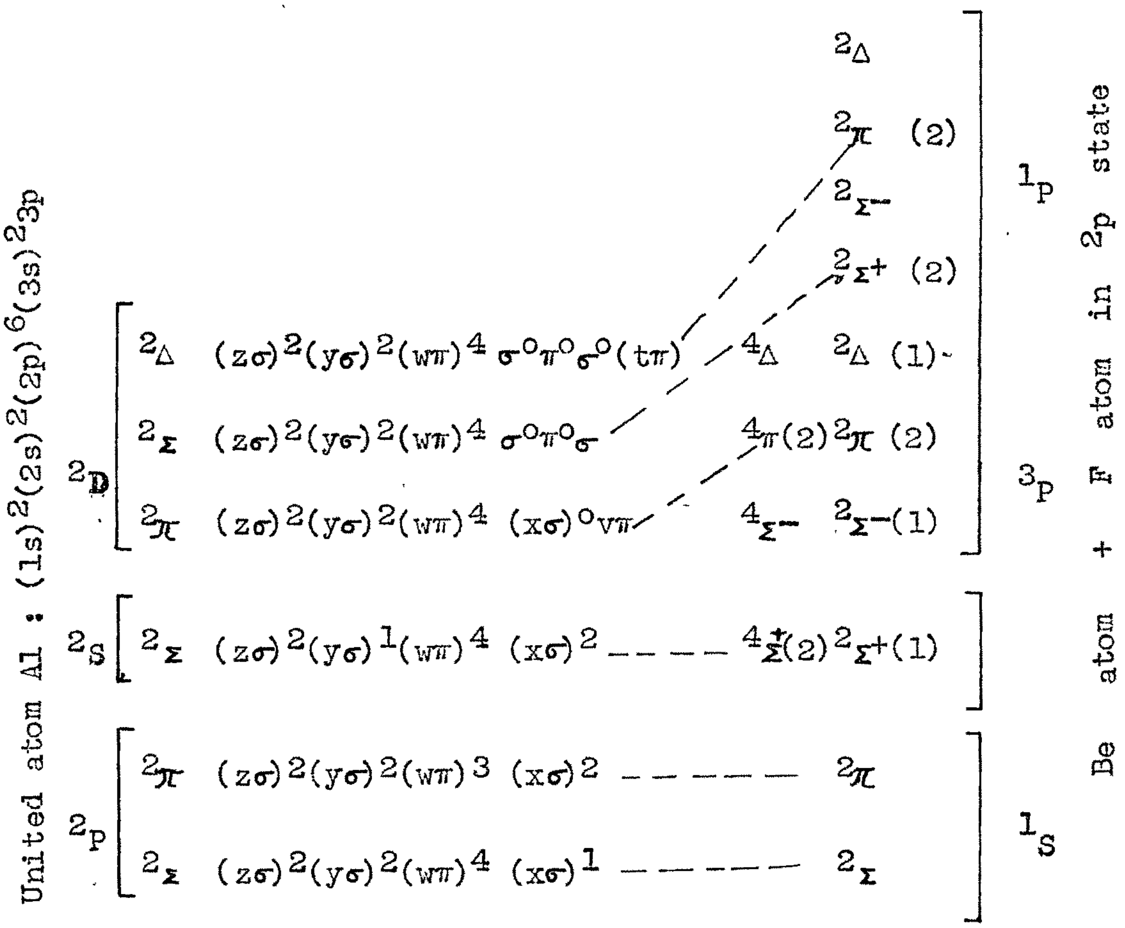
On the other hand a procedure analogous to that for atoms, is employed in which the individual electrons are added one after the other to the nuclei and these electrons occupy themselves certain orbitals. The different arrangements of the electrons (electron configurations) then give the possible molecular states.

The band spectra associated with the halides of mercury, obtained in the present investigation may be interpreted in terms of the electron configurations of the states involved. A careful study of probable states will provide some information about the fragmentary systems observed here. A diatomic mercury halide molecule in its ground state may be expected to dissociate into Hg($^1S_0$) and the halogen ($^2P_{3/2}$) atoms which are the ground states of the respective atoms. The problem will also be considered from the view point of the united atom model which will be useful for the knowledge of low-lying states. The electronic states of HgX (where X stands for the corresponding halogen atom) molecules are expected to be similar to those of BeF molecule whose electronic states are known from the spectroscopic studies of Howell (1943) and hence the present discussion will be based on it.

The electron configuration of beryllium which has four electrons is known to be $1s^2 2s^2$ and that for fluorine having nine electrons is $1s^2 2s^2 2p^5$. The molecule BeF can be supposed to have been formed by splitting the united atom of aluminium which is known to have its electron configuration $1s^2 2s^2 2p^6 3p$. The correlation between the various states of the BeF molecule and the united aluminium atom is given in Table XXII. The aluminium atom has three states

# TABLE XXII

## CORRELATION OF Be + F ATOMS WITH UNITED ATOM Al



$^2P$, $^2S$ and $^2D$ arising from its electron configuration. The electronic states that result by splitting up of the aluminium atom in its low-lying state are $^2\Sigma$ and $^2\pi$. These two states are expected to lie lowest of all the electronic states of BeF molecule and hence also for the HgX molecule. The $^3P$ and $^1P$ excited electronic states of BeF molecule are related to the excited states $^2S$ and $^2D$ of the aluminium atom. The electronic states of halides of mercury involved in producing the ultraviolet spectra of HgX molecules are expected to be similar to the $^3P$ and $^1P$ states.

The two atoms that form the diatomic molecule of mercury halide belong to two different periods of the periodic table and thus have very different charge. In such a case while assigning the electron configuration to the molecule, it is not necessary to take into account the inner closed shells of the separated atoms (Lennard and Jones, 1929). It is thus sufficient for practical purpose to consider only those electrons which are in the outermost orbitals. The lowest electron configurations for the atoms in the present study are as follows:

Hg: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2$

..... KLMNO $6s^2$

Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$ ..... KL $3s^2 3p^5$

Br: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$ ..... KLM $4s^2 4p^5$

I : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$

..... KLMN $5s^2 5p^5$.

If the molecules HgCl, HgBr and HgI are formed from the normal mercury atom ($^1S_0$) and the respective halide atom in their normal states ($^2P_{3/2}$) then the possible electronic states of the molecules are $^2\Sigma^+$ and $^2\pi$ (Herzberg, 1950) i.e.

$$\left.\begin{array}{l} 6s^2\,{}^1S_g(\text{Hg}) + 3s^2 3p^5(\text{Cl}) \\ 6s^2\,{}^1S_g(\text{Hg}) + 4s^2 4p^5(\text{Br}) \\ 6s^2\,{}^1S_g(\text{Hg}) + 5s^2 5p^5(\text{I}) \end{array}\right\} \longrightarrow {}^2\Sigma^+ \text{ and } {}^2\pi .$$

It was shown from the approach of the united atom model that the $^2\Sigma$ and $^2\pi$ states are the low-lying electronic states. Moreover, the lowermost electronic states of the molecules will usually dissociate into normal atoms. Hence it is reasonable to believe that the $^2\Sigma^+$ and $^2\pi$ are the low-lying states of the halides of mercury.

According to Mulliken's (1932) notation, the lowest electron configuration for the molecules HgCl, HgBr and HgI may be expressed as:

KKLLMNO $(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)$ , $^2\Sigma^+$

KKLLMMNO $(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)$ , $^2\Sigma^+$

KKLLMMNNO $(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)$ , $^2\Sigma^+$

or briefly as $\sigma^2\sigma^2\pi^4\sigma$, $^2\Sigma^+$ .

Thus it may be assumed that the $^2\Sigma^+$ state may in all probability be the $^2\Sigma^+$ state as derived from the combination of a normal mercury atom with a normal halogen atom. As in the case of BeF, if most of the molecular binding is considered as due to the $\pi^4$ group, the first excited low-lying state of the halides of mercury may have the following electron configuration:

$$\sigma^2\sigma^2\pi^3\sigma^2 \; , \; ^2\pi \, .$$

The first excited state is expected to have normal mercury and the halogen atom as the dissociation products. Thus the band systems for these molecules should be due to

$$\sigma^2\sigma^2\pi^3\sigma^2, \; ^2\pi \longrightarrow \sigma^2\sigma^2\pi^4\sigma, \; ^2\Sigma^+$$

in which an electron from the strongly bonding $(w\pi)$ orbital is transferred to the antibonding $(x\sigma)$ orbital and consequently one can expect the vibrational frequency of the upper $^2\pi$ state to be less than that of the lower $^2\Sigma^+$ state. Thus the observed bands should have their shading towards red. Although such band systems for the halides of zinc and cadmium are observed (Wieland, 1929, Ternin, 1927; Oeser, 1935 and Ramsastry, 1946), no such system is known for the halides of mercury. As the mercury halides are heavier than the halides of zinc and cadmium, their band systems should shift to the longer wavelengths. Hence even if such a system exists for mercury halides it may perhaps lie in the near infrared region.

The next excited state having a low energy may be represented by $(z\sigma)^2(y\sigma)^1(w\pi)^4(x\sigma)^2$, $^2\Sigma$ in which the transfer of an electron from an inner $(y\sigma)$ orbital to an outer $(x\sigma)$ orbital should produce a reduction in the vibrational frequency. The analyses of the visible bands for halides of mercury were reported by Wieland (1939, 1941 and 1948) and it was observed that the $\omega_e'$ values are less than the corresponding $\omega_e''$ for the respective molecules. The analogous visible band systems for halides of zinc and cadmium also show that $\omega_e' < \omega_e''$ (Patel and Patel, 1966, 1967 and Patel and Rajan, 1967). These groups of bands associated with the halides of Zn, Cd and Hg are attributed to an electronic transition ${}^2\Sigma^+ \longrightarrow {}^2\Sigma^+$.

Now consider the mercury atom in its first excited state and the halogen atom in its normal state. This will give rise to the following molecular states:

$$6s6p\ {}^3P_u(\mathrm{Hg}) + 5s^2 5p^5\ {}^2P_u(\mathrm{halogen}) \longrightarrow$$

$$\Sigma^+(2),\ \Sigma^-, \pi(2) \text{ and } \Delta,$$

out of which only those allowed by selection rules and transition probability considerations should be considered. The molecule in these states should dissociate into ${}^3P(\mathrm{Hg})$ and ${}^2P(\mathrm{halogen})$ atoms.

The next excited state of the mercury halides responsible for the C and D systems is believed to be a ${}^2\pi$ state and these systems are found to occur in the vicinity of the ${}^3P-{}^1S$ resonance line of mercury at 2536.5 A°. This ${}^2\pi$ state may be one of the above anticipated ${}^2\pi$ states. In terms of electron configuration, this state may be shown as

$$\sigma^2 \sigma^2 \pi^4 \sigma^0 \pi\ ,\ {}^2\pi_r$$

having ${}^3P(\mathrm{Hg})$ and ${}^2P(\mathrm{halogen})$ as the dissociation products.

As mentioned earlier, if we consider all the binding strength due to the $\pi^4$ group electron the last $\pi$ is slightly bonding and hence increases the vibrational frequency; although this increase depends upon the strength of the bonding of the electron. It is found from the observed spectra of mercury halides that the upper state frequency is more than the ground state frequency which supports the above expectation. The remaining $^2\pi$ and $^2\Sigma^+$ states may be repulsive.

The other excited molecular states for halides of mercury may result from the excited mercury ($^1P_u$) atom and the normal halogen ($^2P_u$) atom as follows:

$$^1P_u(\mathrm{Hg}) + {}^2P_u(\mathrm{halogen}) \longrightarrow {}^2\Sigma^+\ (2),\ {}^2\Sigma^-,\ {}^2\pi(2) \text{ and } {}^2\Delta$$

out of which only four states, $^2\Sigma^+$ (2) and $^2\pi$ (2) are worth considering. The various far ultraviolet band systems observed for mercury iodide molecule may be attributed to the electronic transitions predicted as above. As in the case of ZnI and CdI, the E system of HgI may be correlated with the $^1P-{}^1S$ resonance line of mercury atom. The bands of E system of HgI resemble in appearance to those of the E systems of ZnI and CdI. In view of this, it may be justifiable to assign a $^2\Sigma$ — $^2\Sigma$ transition to this system of mercury iodide instead of $^2\pi$ — $^2\Sigma$. The upper state $^2\Sigma$ may have an electron configuration in this case as

$$\sigma^2\sigma^2\pi^4(x\sigma)^0(v\pi)^0(u\sigma)^1,\ ^2\Sigma.$$

The transfer of an electron from $(x\sigma)$ orbital to $(u\sigma)$ orbital should produce decrease in the frequency of the upper state. The degradation of the bands towards longer wavelengths supports to believe that the transition involved is as anticipated above. As the other band systems of HgI molecule are not included in the present study their electron configurations are not discussed.

One may expect band systems in far ultraviolet for mercury chloride and mercury bromide molecules analogous to those for mercury iodide molecule. The existance of $^2\Sigma$ — $^2\Sigma$ systems for HgBr is known (Rao and Rao, 1944). Further, in the present study a group of bands associated with HgBr molecule is analysed and designated as D' system. The probable electronic transition for this system may be $^2\Sigma$ — $^2\Sigma$, the upper state may be the same as expected from the combination $^1P_u(Hg)$ + $^2P_u(Br)$. The red degraded bands mixed up with the C system in the case of HgCl molecule may be arising due to a transition in which the upper state involved may result from the above combination.

## CONCLUSIONS:

The results obtained from the present study are summarised here and various electronic states of the halides of mercury are correlated with those for the halides of zinc and cadmium as they belong to the same group (IIb) of the periodic table.

Wieland's class II bands of HgCl and HgBr lying in the region 2900-2650 A° are reinvestigated in the present study. The analyses of the bands forming C systems of these molecules show that the lower state vibrational frequencies obtained are equal to the ground state frequencies of the respective molecules. The C system of HgCl molecule is considered as one of the components of a $^2\pi \longrightarrow {}^2\Sigma$ electronic transition, the other component of the transition is lying in the region 2650-2380 A°. The $^2\pi$ interval in the present case is observed to be 3895 $cm^{-1}$. Similarly the bands of mercury bromide molecule in the region 2968-2789 A° are reanalysed. They are attributed to an electronic transition $^2\pi_{\frac{1}{2}} - {}^2\Sigma$, the $^2\pi_{3/2} - {}^2\Sigma$ component being in the farther ultraviolet region. The doublet separation observed between the C and D systems of HgBr is equal to 3852 $cm^{-1}$.

Thus the $^2\pi$ intervals observed in the present investigation for HgCl and HgBr molecules are inkeeping with the values reported earlier for HgF (Howell, 1943) and HgI (Rao et al., 1944). This order of $^2\pi$ intervals is fairly in good agreement with the theoretically prodicted value. It is concluded from this that the C and D systems of halides of mercury are analogous and electronic transition $^2\pi$ — $^2\Sigma$ involved is related to the $^3P-^1S$ transition in mercury atom. Further, the $^2\pi$ separation observed here can be correlated with those of the halides of zinc and cadmium and such a correlation is given in Table XXIII.

TABLE XXIII

$^2\pi$ INTERVALS FOR THE HALIDES OF Zn,Cd AND Hg

| Metal | F | Cl | Br | I | Theoretical value |
|---|---|---|---|---|---|
| Zn | 370 | 385 | 408 | 389 | 386 |
| Cd | - | 1115 | 1158 | 1300 | 1140 |
| Hg | 3940 | 3896 | 3852 | 3538 | 4295 |

It is obvious from the table that the magnitude of the doublet width in the present study for the halides of mercury is sufficiently large and hence it can be concluded that the electronic transition $^2\pi$ — $^2\Sigma$ in this case belongs to purely Hund's case (a).

The red degraded bands of HgCl molecule mixed up with the C system may be considered as belonging to an an altogether different transition. Further, the double headed bands of HgBr molecule designated as D' system may be attributed to a probable electronic transition $^2\Sigma$ — $^2\Sigma$ having an appreciable spin splitting in the upper state.

The E system of HgI molecule is reinvestigated in the present study. The analysis shows that all the observed bands could be arranged to form a single system. The lower state frequency observed here is the ground state frequency of the HgI molecule. The system resembles to the E systems of ZnI and CdI molecules. It is observed that the origin of the E system of HgI is shifted towards the longer wavelength side of that of the CdI molecule and the latter one is again shifted towards the longer wavelength side of that of the ZnI molecule. Such a trend of shifting of the system origin towards red with the increase in the mass of similar molecules is well known and hence the system origin suggested for the E system of HgI in the present study is justifiable. The system is ascribed to an electronic transition $^2\Sigma \longrightarrow {}^2\Sigma$.

The vibrational frequencies derived from the present investigation have been collected in Table XXIV. It is to be expected that as the mass of the halogen increases, the value of the vibrational constant $\omega_e$ should decrease. As is clear from the table such a trend is observed here in the case of both the excited and ground state frequencies.

A comparison of the various electronic states of halides of mercury with the corresponding states of halides of zinc and cadmium is shown in Fig. 5. The atomic states $^3P$ and $^1P$ of the corresponding metal atoms are also given to demonstrate how closely the molecular states follow them.

As the atoms Zn, Cd and Hg belong to the same group of the periodic table, their halide spectra are expected to show some similarity in appearance and among their spectroscopic properties. The vibrational constants for the electronic states of halides of mercury studied here are compared with the vibrational constants for the corresponding states of the halides of zinc and cadmium and are given in Table XXV.

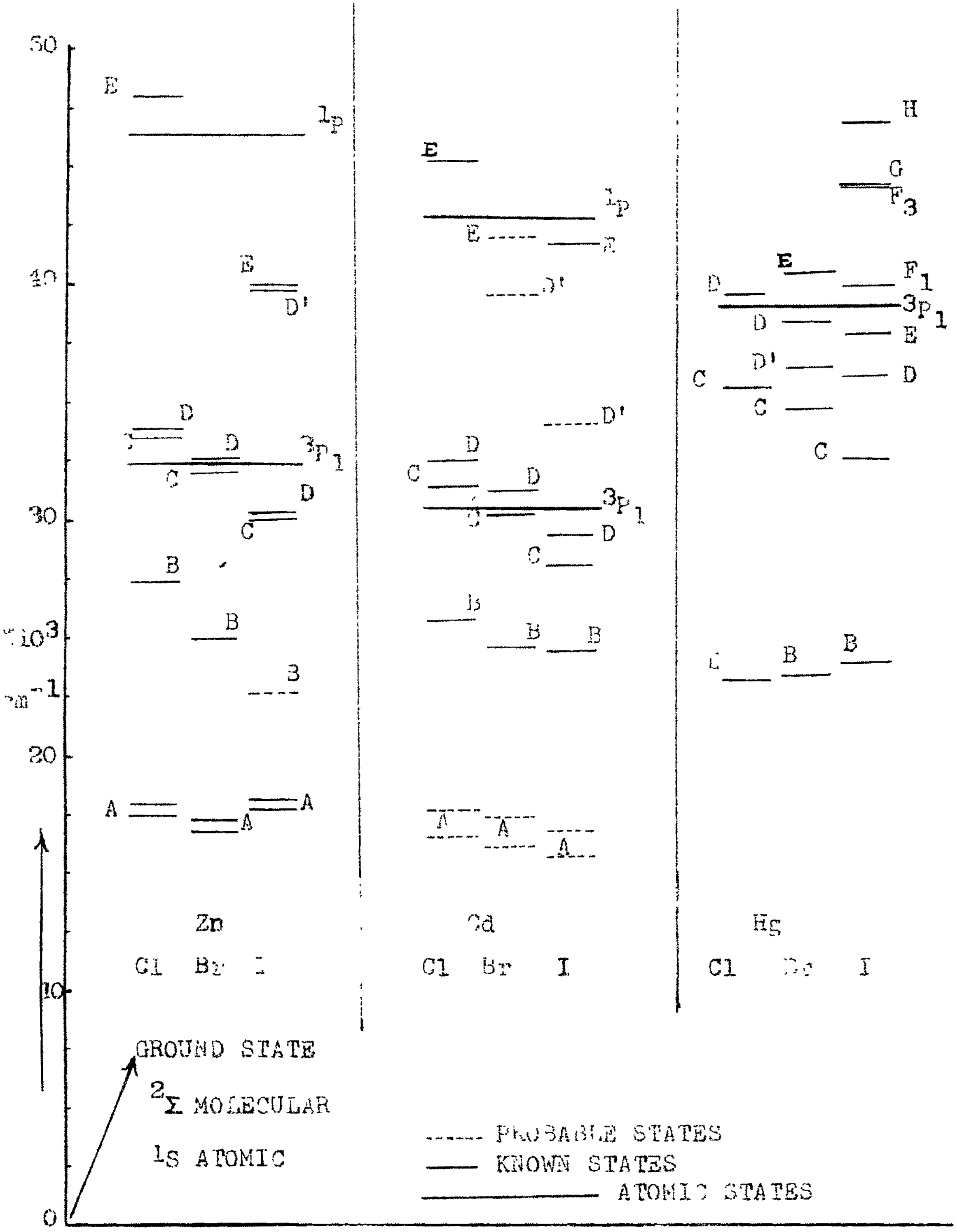


FIG. 5

ENERGY LEVEL DIAGRAM FOR THE HALIDES OF Zn, Cd AND Hg

# TABLE XXIV

## CONSTANTS DERIVED FROM THE PRESENT STUDY

### (i) VIBRATIONAL CONSTANTS:

| Molecule | Transition | Region | $\nu_{o,o}$ | $\omega_e'$ | $\omega_e'x_e'$ | $\omega_e''$ | $\omega_e''x_e''$ |
|---|---|---|---|---|---|---|---|
| HgCl | $^2\pi_{\frac{1}{2}} - {}^2\Sigma$ | 2919-2660 | 35831.7 | 382.00 | 1.00 | 292.60 | 1.45 |
| HgBr | $^2\pi_{\frac{1}{2}} - {}^2\Sigma$ | 2968-2766 | 34767.6 | 278.64 | 1.82 | 187.29 | 0.96 |
| HgBr | $^2\pi_{\frac{3}{2}} - {}^2\Sigma$ | 2789-2694 | 36506.6 | 233.80 | 1.68 | 184.05 | 1.15 |
| HgBr | $^2\Sigma - {}^2\Sigma$ | 2470-2440 | 40626.0 | 170.42 | 0.71 | 186.02 | 0.96 |
| HgI | $^2\Sigma - {}^2\Sigma$ | 2651-2533 | 38511.0 | 79.96 | 0.45 | 126.16 | 1.01 |

### (ii) ROTATIONAL CONSTANTS FOR THE THREE BANDS OF $^2\pi_{3/2} \rightarrow {}^2\Sigma$ SYSTEM OF HgCl MOLECULE:

| v',v" | Band origin | $B_v'$ | $B_v''$ | r' $10^{-8}$ cm. | r" $10^{-8}$ cm. | I' $10^{-40}$ $gmcm^2$ | I" $10^{-40}$ $gmcm^2$ |
|---|---|---|---|---|---|---|---|
| 0,1 | 39439.9 | 0.1114 | 0.1029 | 2.253 | 2.345 | 251.5 | 271.9 |
| 0,2 | 39152.2 | 0.1124 | 0.1024 | $2.24_2$ | 2.350 | 248.9 | 273.2 |
| 1,3 | 39207.6 | 0.0985 | 0.0913 | 2.239 | 2.490 | 284.0 | 306.4 |

## TABLE XXV

## VIBRATIONAL FREQUENCIES OF HALIDES OF Zn, Cd AND Hg

| State | Metal | F | Cl | Br | I |
|---|---|---|---|---|---|
| X | Zn | (630) | 390.5 | 266* | 223.4 |
|  | Cd | (536) | 330.5 | 230.0 | 178.5 |
|  | Hg | 490.8 | 292.6* | 186.25* | 125.6* |
| C | Zn | (599) | 384.0 | (250) | 248.2 |
|  | Cd | - | 399 | 254.5 | 186.36 |
|  | Hg | (506) | 382.00* | 278.64* | 235.6 |
| D | Zn | (599) | 381.8 | (250) | 211.7 |
|  | Cd | - | (399) | 254.5 | 196.6 |
|  | Hg | 469.4 | 341.4 | 228.5 | 178.0 |
| E | Zn | - | - | - | 142.5 |
|  | Cd | 535 | 247.9 | - | 108.5 |
|  | Hg | - | - | 170.42* | 79.96* |

(The constants collected here are taken from Herzberg(1950) except those which are marked by asterisk. The value for ground state of ZnBr is from Jacob Rajan (1967) and the values for the C systems of HgCl and HgBr and the E system of HgBr and HgI are from the present study).

The comparison shows a decrease in the corresponding frequencies with increasing heavyness of the molecule,which is a general characteristic of the spectroscopic properties of the molecules.

In view of the theoretically predicted first excited state $^2\pi$, a reinvestigation of the visible spectra of halides of mercury may prove fruitful. Attempts in this direction are in progress and definite results have been obtained in the study of the spectra of iodides of cadmium and zinc. In the analysis reported by Wieland (1939, 1941, 1960) for the visible bands of HgCl and HgBr, a number of violet degraded bands have been assigned to the same system consisting of red degraded bands. A detailed investigation of these bands is planned as a future programme in this laboratory.

# APPENDIX

## SPECTRA OF CADMIUM IODIDE MOLECULE

The purpose of including an appendix to the thesis was to verify the results and conclusion arrived at from the present study on the spectra of halides of mercury. The near ultraviolet spectrum of cadmium iodide molecule was selected to fulfill the above desire. The C system of CdI molecule analysed completely for the first time is reported here. The visible spectrum obtained along with the near ultraviolet bands is analysed and the results obtained from it are also presented.

### (i) BAND SPECTRUM OF CdI MOLECULE IN THE REGION 3586-3495 A° (C-SYSTEM):

Wieland (1929) analysed the D system of CdI molecule with the (0,0) band at 3384 A°. He also reported three bands at 3586, 3563 and 3541 A°, the last being strongest of all. It was suggested by Howell (1943) that if these two groups of bands form two components of a $^2\pi \longrightarrow {}^2\Sigma$ electronic transition with their (0,0) bands at 3384 and 3541 A° respectively, a doublet interval of about 1300 $cm^{-1}$ could be obtained which was not considered so close to the anticipated value of 1140 $cm^{-1}$; it was however of the right order. The work was repeated by Ramsastry and Rao (1946) who listed a few additional bands on the shorter wavelength side and also observed the above mentioned three bands and assigned them to the missing component of the above transition (C system). However, the vibrational constants of the C system could not be derived by them as only three bands were observed by them. Hence it was thought desirable to photograph this spectrum with better details and to give the complete vibrational analysis of the bands. This study was then expected to provide an information about the $^2\pi$ interval between the C and D systems of CdI molecule and verify whether the correlation of $^2\pi$ interval for halides of mercury with it can be established or not.

The spectrum of CdI molecule was excited in a quartz discharge tube using the same experimental set up as employed in the present study. The discharge tube was continuously evacuated by a high vacuum pump and the discharge was established by a 125 watts high frequency oscillator. The bands developed better in a characteristic golden yellowish colour of the discharge. A careful and controlled heating in order to maintain the above conditions of the discharge was found necessary. The spectra were recorded on a two metre plane grating spectrograph at a dispersion of 7.35 A°/mm. Ilford N30 and N40 plates were employed and exposures of about an hour were found adequate to record the spectra. Iron arc spectrum was used to determine the wavelengths.

The band spectrum of CdI molecule in the region 3620-3465 A° is reproduced in plate $A_1$ and some of the prominent bands are marked on it. The vibrational structure of the (0,0), (0,1) and (0,2) bands is clearly seen in the spectrogram. The relative intensities, wavelengths, wave numbers in vacuum and vibrational assignments are given in Table $A_1$. The wave numbers reported by Ramsastry (1946) are given in the last column.

In analysing the bands it was assumed that the structure accompanying the three prominent bands was the vibrational structure of the system and not the rotational structure of a single band. This conclusion was arrived at by the following reasons:

(i) The molecule is sufficiently heavy and with the dispersion used it was not possible to resolve the rotational structure.

(ii) The vibrational constants of the two states involved are very near to each other and as such, the shading of the bands will not be prominent. The same feature has been observed in the case of D system also.

(iii) Some of the higher members of the D system mix with the C system and give a misleading appearance of long and extensive degration to the violet under low dispersion.

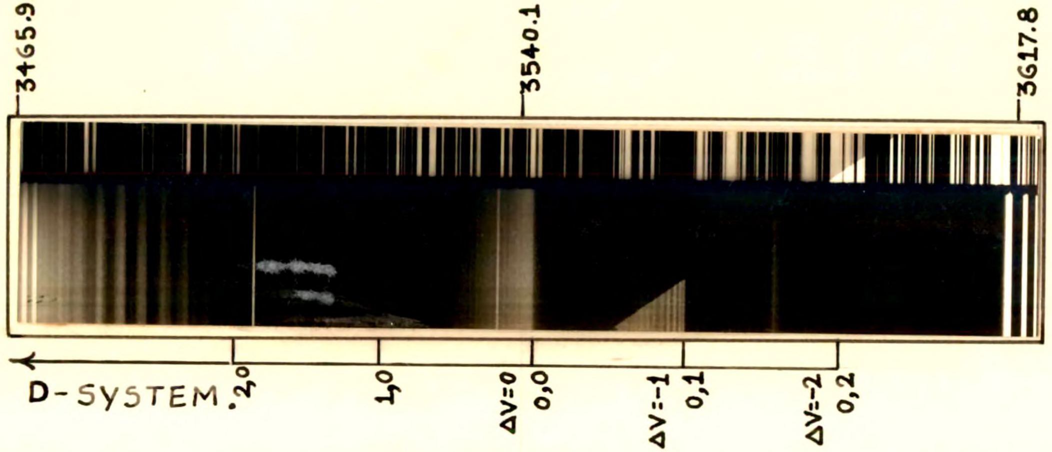


PLATE. A1

SPECTROGRAM OF CdI TAKEN AT
A DISPERSION OF 7.35 A°/ M. M.
C-SYSTEM.

## TABLE $A_1$

## BAND HEAD DATA ON CdI MOLECULE (C-SYSTEM)

| Intensity | Wave length $\lambda$ A° | Wave number in vacuum $\nu$ cm$^{-1}$ | Assignment (v',v") | $\nu_{obs} - \nu_{cal}$ | Value given by Ramsastry |
|---|---|---|---|---|---|
| 2 | 3585.85 | 27879.4 | 0,2 | 0.0 | 27880.2 |
| 2 | 3584.52 | 27889.8 | 1,3 | 0.1 | |
| 2 | 3583.27 | 27899.5 | 2,4 | -0.4 | |
| 2 | 3582.30 | 27907.1 | 3,5 | -2.9 | |
| 2 | 3580.94 | 27917.6 | 4,6 | -2.6 | |
| 1 | 3579.35 | 27930.1 | 5,7 | 0.6 | |
| 1 | 3578.22 | 27938.9 | 6,8 | -0.2 | |
| 1 | 3576.99 | 27949.1 | 7,9 | 0.6 | |
| 1 | 3575.92 | 27956.9 | 8,10 | -0.8 | |
| 1 | 3574.67 | 27966.7 | 9,11 | -0.1 | |
| 4 | 3563.36 | 28055.4 | 0,1 | 0.2 | 28054.5 |
| 4 | 3562.20 | 28064.6 | 1,2 | 0.2 | |
| 4 | 3561.12 | 28073.1 | 2,3 | -0.3 | |
| 4 | 3560.18 | 28080.5 | 3,4 | -1.7 | |
| 4 | 3558.99 | 28089.9 | 4,5 | -1.0 | |
| 3 | 3557.82 | 28099.1 | 5,6 | -0.3 | |
| 3 | 3556.53 | 28109.3 | 6,7 | 1.6 | |
| 3 | 3555.69 | 28115.9 | 7,8 | 0.0 | |

Contd...

## TABLE $A_1$ (contd.)

| Intensity | Wave length $\lambda$ A° | Wave number in vacuum $\nu$ $cm^{-1}$ | Assignment (v',v") | $\nu_{obs}-\nu_{cal}$ | Value given by Ramsastry |
|---|---|---|---|---|---|
| 2 | 3554.77 | 28123.2 | 8,9 | -0.8 | |
| 10 | 3541.03 | 28232.3 | 0,0 | 0.0 | 28232.9 |
| 10 | 3540.00 | 28240.5 | 1,1 | 0.3 | |
| 10 | 3539.20 | 28246.9 | 2,2 | -1.1 | |
| 9 | 3538.11 | 28255.6 | 3,3 | -0.1 | |
| 9 | 3537.32 | 28261.9 | 4,4 | -1.2 | |
| 8 | 3536.25 | 28270.4 | 5,5 | 0.0 | |
| 8 | 3535.32 | 28277.9 | 6,6 | 0.3 | |
| 7 | 3534.49 | 28284.5 | 7,7 | -0.1 | |
| 7 | 3533.02 | 28296.9 | 9,9 | -1.2 | |
| 3 | 3517.98 | 28417.3 | 1.0 | 0.0 | |
| 2 | 3517.15 | 28424.0 | 2,1 | 0.1 | |
| 2 | 3495.29 | 28601.8 | 2,0 | 0.9 | |

Taking the above aspects into consideration, the bands were analysed and following quantum equation was derived:

$$\nu_{\text{head}} = 28228.25 + \left[186.36(v'+\tfrac{1}{2}) - 0.68(v'+\tfrac{1}{2})^2\right] - \left[178.25(v''+\tfrac{1}{2}) - 0.60(v''+\tfrac{1}{2})^2\right]$$

The values of $(\nu_{\text{obs.}} - \nu_{\text{cal.}})$ given in column 5 of Table $A_1$ indicate a close agreement. The bands, when arranged in Deslandres table as given in Table $A_2$, show a nice regularity of intervals. As only three sequences are developed, the Condon parabola is observed to be very narrow. As suggested by Howell (1943) the system has been ascribed to a transition $^2\pi - {}^2\Sigma$ whose other component is the D system of the molecule. The doublet interval observed in the present analysis is 1300 $\text{cm}^{-1}$. This order of the $^2\pi$ interval for CdI is of the anticipated order.

The magnitude of the $^2\pi$ interval related to the $^3P$ width of the respective metal atoms of mercury, cadmium and zinc show some regularity as the intervals decrease with decrease in atomic weight of the corresponding metal atom.

During the course of above study on the near ultraviolet spectrum of CdI molecule an extensive group of red

## TABLE $A_2$

### DESLANDRES TABLE FOR C-SYSTEM OF CdI BANDS

| v' \ v" | 0 | | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | | 7 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 28232.3(10) | 176.9 | 28055.4(4) | 176.0 | 27879.4(2) | | | | | | | | | | |
| | 185.0 | | 185.1 | | 185.2 | | | | | | | | | | |
| 1 | 28417.3(3) | 176.8 | 28240.5(10) | 173.9 | 28064.6(4) | 174.8 | 27889.8(2) | | | | | | | | |
| | 184.5 | | 183.5 | | 182.3 | | 183.3 | | | | | | | | |
| 2 | 28601.8(2) | 177.8 | 28424.0(2) | 177.1 | 28246.9(10) | 173.8 | 28073.1(4) | 173.6 | 27899.5(2) | | | | | | |
| | | | | | | | 182.5 | | 181.0 | | | | | | |
| 3 | | | | | | | 28255.6(9) | 175.1 | 28080.5(4) | 173.4 | 27907.1(2) | | | | |
| | | | | | | | | | 181.4 | | 182.8 | | | | |
| 4 | | | | | | | | | 28261.9(9) | 172.0 | 28089.9(4) | 172.3 | 27917.6(2) | | |

degraded bands was observed in the visible region on the negatives. The analysis of these bands in the region 4100-4800 A° was far from complete. Hence it was of interest to study these bands in detail.

## (ii) VISIBLE SYSTEM OF CdI MOLECULE:

The knowledge about the ultraviolet spectra of CdI molecule is fairly good whereas limited information is available about its spectrum in the visible region. Bands in the region 6600-3600 A° reported by Wieland(1929) were diffuse, line-like and appeared on a continuum with a pronounced intensity maximum at 6500 A°. Ramsastry and Rao (1946) obtained these bands in a transformer discharge and attempted an analysis but the lower state frequency reported by them did not agree well with the ground state frequency of the CdI molecule. In view of this,the present supplimentary investigation was undertaken. The results obtained are reported here.

The visible spectrum of CdI molecule was excited under the conditions mentioned in the earlier part of the appendix. The visible bands were photographed along with the C system on a plane grating spectrograph in the first order having a dispersion of 7.3 A°/mm. Exposures of about twenty five minutes were found adequate to produce satisfactory spectrograms. A part of the spectrum extending from 4300-4800 A° is reproduced in Plate $A_2$. The bands are clearly degraded to red. In Table $A_3$, visually estimated intensities, wave numbers in vacuum and the assignments of the band heads in the region 4100-4800 A° are given.

A clue to the analysis was obtained when the bands in the region 4300-4800 A° were arranged in arrays and and the differences determined. One of the striking features which has been observed in the present investigation is the fact that these bands lie over two continua extending from 3600-4900 A° and from 5300-6500 A° with their intensity maxima respectively at 4500 A° and 6500 A°. The present analysis is therefore based on the assumption that the bands in the two regions mentioned above form separate systems. This has been further verified by evaluating the intervals amongst the bands in the respective regions.

A few long v' progressions were then picked out and a regular decrease of interval from 177 $cm^{-1}$ was found amongst most of the intense and sharp bands of these groups. A systematic vibrational analysis was then followed up and the vibrational constants of the upper and lower electronic transition were determined. The following vibrational

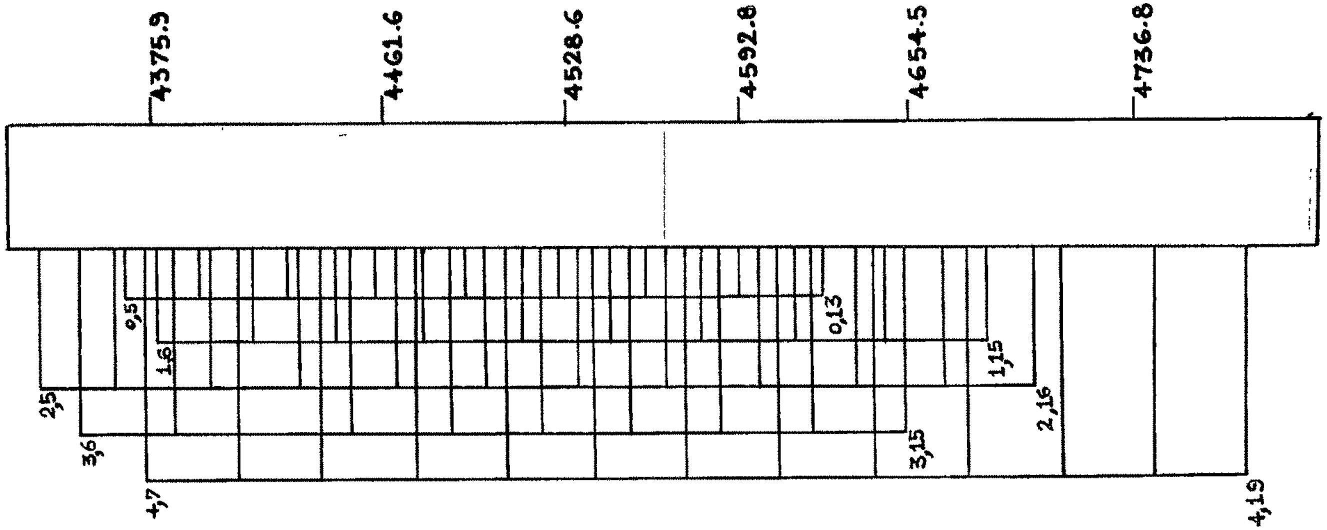


PLATE . $A_2$.

SPECTROGRAM OF CdI TAKEN AT
A DISPERSION OF 7.3 A°/ M. M.
B- SYSTEM.

## TABLE $A_3$

## BAND HEAD DATA ON CdI MOLECULE (B-SYSTEM)

| Intensity | Wavelength $\lambda$ A° | Wave number in vacuum $\nu$ cm$^{-1}$ | Assignment (v',v") | $\nu_{obs} - \nu_{cal}$ |
|---|---|---|---|---|
| 2 | 4793.67 | 20855 | 6,20 | -6.0 |
| 2 | 4780.26 | 20913 | 4,19 | 2.0 |
| 2 | 4772.56 | 20948 | 8,20 | -0.6 |
| 2 | 4769.00 | 20963 | 5,19 | -2.1 |
| 1 | 4764.91 | 20981 | 9,20 | -5.9 |
| 3 | 4756.50 | 21018 | 6,19 | 2.9 |
| 1 | 4748.61 | 21053 | 11,20 | -2.8 |
| 4 | 4746.61 | 21062 | 7,19 | 0.9 |
| 3 | 4744.40 | 21072 | 4,18 | 5.2 |
| 4 | 4737.30 | 21103 | 8,19 | -0.1 |
| 4 | 4731.60 | 21121 | 5,18 | 0.2 |
| 2 | 4729.50 | 21138 | 9,19 | -3.1 |
| 5 | 4722.77 | 21168 | 6,18 | -2.4 |
| 4 | 4721.23 | 21175 | 10,19 | -0.1 |
| 3 | 4715.00 | 21203 | 11,19 | -2.1 |
| 4 | 4711.74 | 21218 | 7,18 | 1.2 |
| 4 | 4709.77 | 21226 | 4,17 | 2.3 |
| 4 | 4702.58 | 21259 | 8,18 | -0.2 |
| 5 | 4697.66 | 21281 | 5,17 | 3.3 |

Contd...

## TABLE $A_3$ (Contd.)

| Intensity | Wavelength $\lambda$ A° | Wave number in vacuum $\nu$ cm$^{-1}$ | Assignment (v',v") | $\nu_{obs} - \nu_{cal}$ |
|---|---|---|---|---|
| 4 | 4695.80 | 21290 | 9,18 | -6.0 |
| 5 | 4688.12 | 21325 | 6,17 | -2.7 |
| 5 | 4681.44 | 21355 | 1,15 | -0.1 |
| 5 | 4677.45 | 21373 | 7,17 | -0.7 |
| 5 | 4675.01 | 21384 | 4,16 | 2.2 |
| 4 | 4668.08 | 21416 | 8,17 | 0.3 |
| 5 | 4667.01 | 21421 | 2,15 | -0.1 |
| 6 | 4664.11 | 21434 | 5,16 | -1.8 |
| 6 | 4654.43 | 21479 | 3,15 | -4.1 |
| 6 | 4652.54 | 21488 | 6,16 | 2.2 |
| 7 | 4645.60 | 21520 | 1,14 | 4.4 |
| 5 | 4643.17 | 21531 | 7,16 | 0.8 |
| 5 | 4640.77 | 21542 | 4,15 | 0.9 |
| 5 | 4633.60 | 21574 | 8,16 | 0.2 |
| 7 | 4632.10 | 21582 | 2,14 | 0.4 |
| 7 | 4629.39 | 21595 | 5,15 | 0.1 |
| 7 | 4628.06 | 21601 | 0,13 | -6.2 |
| 4 | 4624.66 | 21617 | 9,16 | 5.2 |
| 6 | 4618.56 | 21646 | 3,14 | 2.4 |

Contd...

TABLE $A_3$ (Contd.)

| Intensity | Wavelength $\lambda$ A° | Wave number in vacuum $\nu$ cm$^{-1}$ | Assignment (v',v") | $\nu_{obs} - \nu_{cal}$ |
|---|---|---|---|---|
| 9 | 4611.50 | 21679 | 1,13 | 1.9 |
| 6 | 4608.41 | 21692 | 7,15 | 0.9 |
| 7 | 4605.47 | 21707 | 4,14 | 5.4 |
| 5 | 4599.81 | 21734 | 8,15 | 0.9 |
| 8 | 4598.50 | 21740 | 2,13 | -3.2 |
| 7 | 4595.78 | 21753 | 5,14 | -2.6 |
| 8 | 4591.18 | 21774 | 0,12 | 4.0 |
| 7 | 4584.82 | 21805 | 3,13 | -0.2 |
| 10 | 4577.60 | 21840 | 1,12 | 0.0 |
| 6 | 4576.06 | 21847 | 7,14 | -4.6 |
| 9 | 4572.46 | 21864 | 4,13 | 0.8 |
| 6 | 4566.20 | 21893 | 8,14 | -0.6 |
| 9 | 4563.57 | 21906 | 2,12 | 0.0 |
| 9 | 4558.40 | 21931 | 0,11 | -1.0 |
| 9 | 4550.50 | 21969 | 3,12 | 1.0 |
| 9 | 4543.57 | 22003 | 1,11 | -1.0 |
| 10 | 4538.49 | 22027 | 4,12 | 1.0 |
| 9 | 4530.46 | 22067 | 2,11 | -3.0 |
| 10 | 4524.10 | 22098 | 0,10 | -1.8 |

Contd....

## TABLE $A_3$ (Contd.)

| Intensity | Wavelength $\lambda$ A° | Wave number in vacuum $\nu$ $cm^{-1}$ | Assignment (v',v") | $\nu_{obs} - \nu_{cal}$ |
|---|---|---|---|---|
| 10 | 4516.94 | 22133 | 3,11 | 1.0 |
| 10 | 4509.09 | 22171 | 1,10 | 1.8 |
| 10 | 4505.44 | 22189 | 4,11 | -1.0 |
| 9 | 4497.10 | 22230 | 2,10 | -5.2 |
| 9 | 4490.76 | 22262 | 0,9 | -3.5 |
| 10 | 4484.80 | 22291 | 3,10 | -6.2 |
| 9 | 4474.65 | 22342 | 1,9 | 6.5 |
| 9 | 4472.15 | 22355 | 4,10 | -0.2 |
| 9 | 4463.40 | 22398 | 2,9 | -3.6 |
| 8 | 4456.92 | 22431 | 0,8 | -2.1 |
| 8 | 4449.25 | 22470 | 3,9 | 6.5 |
| 8 | 4442.40 | 22503 | 1,8 | -0.1 |
| 7 | 4438.86 | 22522 | 4,9 | 0.4 |
| 4 | 4434.18 | 22546 | 8,10 | -1.2 |
| 9 | 4428.65 | 22574 | 2,8 | 4.9 |
| 7 | 4424.07 | 22597 | 0,7 | -4.8 |
| 7 | 4417.48 | 22631 | 3,8 | -0.1 |
| 7 | 4409.73 | 22671 | 1,7 | -0.8 |

Contd....

## TABLE $A_3$ (Contd.)

| Intensity | Wavelength $\lambda$ A° | Wave number in vacuum $\nu$ $cm^{-1}$ | Assignment (v',v") | $\nu_{obs} - \nu_{cal}$ |
|---|---|---|---|---|
| 7 | 4406.11 | 22689 | 4,8 | -0.1 |
| 3 | 4401.14 | 22715 | 8,9 | 1.4 |
| 7 | 4395.46 | 22744 | 2,7 | 6.2 |
| 5 | 4390.51 | 22770 | 0,6 | -1.7 |
| 6 | 4384.80 | 22800 | 3,7 | 0.2 |
| 5 | 4376.38 | 22843 | 1,6 | 1.3 |
| 5 | 4373.60 | 22858 | 4,7 | 0.2 |
| 6 | 4364.70 | 22905 | 2,6 | -2.7 |
| 5 | 4357.85 | 22940 | 0,5 | -2.8 |
| 5 | 4351.10 | 22976 | 3,6 | 6.3 |
| 4 | 4345.94 | 23004 | 7,7 | -3.8 |
| 4 | 4336.65 | 23052 | 8,7 | 2.2 |
| 6 | 4331.94 | 23078 | 2,5 | -0.8 |
| 4 | 4325.64 | 23112 | 0,4 | -3.1 |
| 5 | 4320.12 | 23141 | 3,5 | 0.2 |
| 3 | 4314.27 | 23172 | 7,6 | -5.7 |
| 3 | 4309.10 | 23200 | 4,5 | 1.2 |
| 2 | 4300.17 | 23248 | 5,5 | -4.8 |
| 3 | 4282.10 | 23347 | 7,5 | -1.8 |
| 3 | 4276.39 | 23378 | 4,4 | 6.9 |

Contd...

## TABLE $A_3$ (Contd.)

| Intensity | Wavelength $\lambda$ A° | Wave number in vacuum $\nu$ cm$^{-1}$ | Assignment (v',v") | $\nu_{obs} - \nu_{cal}$ |
|---|---|---|---|---|
| 3 | 4269.44 | 23426 | 5,4 | 0.9 |
| 4 | 4261.20 | 23461 | 10,5 | -1.8 |
| 3 | 4258.60 | 23475 | 6,4 | -0.1 |
| 5 | 4256.70 | 23486 | 3,3 | -0.5 |
| 4 | 4245.10 | 23550 | 4,3 | 5.5 |
| 3 | 4236.67 | 23597 | 5,3 | -1.5 |
| 4 | 4230.30 | 23632 | 10,4 | -3.1 |
| 4 | 4214.90 | 23719 | 4,2 | -0.2 |
| 5 | 4211.56 | 23737 | 8,3 | 0.5 |
| 5 | 4198.89 | 23809 | 10,3 | 0.5 |
| 6 | 4189.60 | 23862 | 7,2 | -7.1 |
| 4 | 4183.84 | 23894 | 4,1 | -1.0 |
| 5 | 4180.89 | 23912 | 8,2 | 0.8 |
| 5 | 4173.79 | 23953 | 5,1 | 4.0 |
| 5 | 4166.71 | 23993 | 6,1 | -6.0 |
| 3 | 4163.90 | 24009 | 11,2 | -4.2 |
| 6 | 4159.00 | 24038 | 7,1 | -7.0 |
| 5 | 4138.30 | 24158 | 10,1 | -1.0 |
| 4 | 4127.90 | 24219 | 7,0 | -3.0 |

quantum equation satisfactorily accounts for the band heads in the region 4130-4800 A°:

$$\nu_{head} = 23868.44 + \left[74.00(v'+\tfrac{1}{2}) - 2.00(v'+\tfrac{1}{2})^2\right] - \left[178.18(v''+\tfrac{1}{2}) - 0.59(v''+\tfrac{1}{2})^2\right]$$

The bands are arranged in a Deslandres table as shown in Table $A_4$. The relative intensities of the bands are given in parentheses. The intensity distribution of the bands follows an open Condon parabola which is a characteristic feature of most of the band systems in visible for the halides of Zn, Cd and Hg.

For the cadmium iodide molecule the low-lying state belongs to an electronic configuration $\sigma^2 \sigma^2 \pi^4 \sigma$, $^2\Sigma^+$ and in all probability is the ground state. The upper electronic state in all probability may be due to an electronic configuration $\sigma^2 \sigma \pi^4 \sigma^2$, $^2\Sigma^+$. The transition $^2\Sigma \longrightarrow {^2\Sigma}$(ground) involving a transition of the electron from an inner $\sigma$ orbital to outer $\sigma$ orbital is consistent with the observed decrease in the vibrational frequency of excited state.

The bands in the red region differ from those in the region 4100 A° in number of respects. They are line-like and the degradation is not extensive. That these bands are

## TABLE $A_4$

## DESLANDRES TABLE FOR B-SYSTEM OF CdI BANDS

| 1 | | 2 | | 3 | | 4 | | 5 | | 6 | | 7 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 23112(4) | 172 | 22940(5) | 170 | 22770(5) | 173 | 22597(7) | 166 |
| | | | | | | | | | | 73 | | 74 | |
| | | | | | | - | | - | | 22843(5) | 172 | 22671(7) | 168 |
| | | | | | | | | | | 62 | | 73 | |
| | | | | | | - | | 23078(6) | 173 | 22905(6) | 161 | 22744(7) | 170 |
| | | | | | | | | 63 | | 71 | | 56 | |
| | | | | 23486(5) | | - | | 23141(5) | 615 | 22976(5) | 176 | 22800(6) | 169 |
| | | | | 64 | | | | 59 | | | | 58 | |
| 23894(4) | 175 | 23719(4) | 169 | 23550(4) | 172 | 23378(3) | 178 | 23200(3) | | | | 22858(5) | 169 |

TABLE $A_4$ (Contd.)

| v' \ v" | 10 | | 11 | | 12 | | 13 | | 14 | | 15 | | 16 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 22098(10) | 167 | 21931(9) | 157 | 21774(8) | 173 | 21601(7) | | - | | | | |
| | 73 | | 72 | | 66 | | 78 | | | | | | |
| 1 | 22171(10) | 168 | 22003(9) | 163 | 21840(10) | 161 | 21679(9) | 159 | 21520(7) | 165 | 21355(5) | | |
| | 59 | | 64 | | 66 | | 61 | | 62 | | 66 | | |
| 2 | 22230(9) | 163 | 22067(9) | 161 | 21906(9) | 166 | 21740(8) | 158 | 21582(7) | 161 | 21421(5) | | - |
| | 61 | | 66 | | 63 | | 65 | | 64 | | 58 | | |
| 3 | 22291(10) | 158 | 22133(10) | 164 | 21969(9) | 164 | 21805(7) | 159 | 21646(6) | 167 | 21479(6) | | - |
| | 64 | | 56 | | 58 | | 59 | | 61 | | 63 | | |
| 4 | 22355(9) | 166 | 22189(10) | 162 | 22027(10) | 163 | 21864(9) | 157 | 21707(7) | 165 | 21542(5) | 158 | 21384(5) |

not due to $I_2$ was verified by recording the emission bands of iodine molecule and making head to head comparison. The carrier of the system has thus been established and detailed investigation of the bands of cadmium iodide in the red region is undertaken.