CHAPTER 5.

VIBRATIONAL ANALYSIS.

In this chapter vibrational analyses of the various band systems of CdCl, CdBr and CdI molecules in the ultra-violet and visible regions which have not been analysed before or which are observed for the first time in the present investigation will be discussed. For some of the band groups, for which accurate measurements were not possible because of their diffuse appearance and low intensity or due to low dispersion spectrographs available in the laboratory, regularities of intervals only, have been pointed out. The detailed analysis of these is under plan and will be taken up shortly when higher dispersion spectrograph will be available in the laboratory.

To avoid unnecessary repeatition the analysis is presented according to the following sequence.

(i) Vibrational analysis of B - systems of CdCl, CdBr and CdI molecules.

(ii) A preliminary analysis of the bands of CdCl, CdBr and CdI molecules in the red region.

(iii) Improvement of the analysis of the ultra-violet systems observed by previous workers.

(iv) A preliminary analysis of the D' systems of CdBr and CdI molecules.

and (v) E systems of CdBr and CdI molecules.

(i) B - systems (Plates 4, 7, 11.)

A clue to the analysis of CdCl bands was obtained from sharp bands obtained in the region $\lambda\lambda$4250-4770 A.U. A decreasing separation ranging from 318 cm^{-1} to 309 cm^{-1} between alternate bands existed for two groups. These groups were assigned to two different v' - progressions. It was possible to get lower state difference of about 330 cm^{-1}. for the lower members of these progressions. The appearance of the bands (Plate 4) in the region λλ3800-4200 A.U. is slightly different as compared to those observed on the longer wavelength side. They are here referred to as group A and group B bands. The appearance of bands in group B is misleading as it suggests a rotational structure of a band. The following reasons have lead the present author to believe that they are due to vibrational structure :

(i) One cannot expect to observe the rotational structure of a heavy molecule like the molecules selected in the present study.

(ii) The rotational spacing must be fairly less in view of the fact that the dispersion is low.

(iii) Since dispersion is low it may give rise to overlapping of the vibrational bands of one sequence with that of the other.

and (iv) When the complete analysis of these molecules is made the results support the evidences presented by earlier workers.

A similar method of sorting out the bands in the case of CdBr (Plate 7) was adopted and it was possible to get the lower state difference of about 230 cm^{-1}.

In the case of the molecule CdI most of the bands consist of two or three components. This feature is more prominent in the region $\lambda\lambda$4400-4800 A.U. (Plate 11). On closer examination it was found that they had different $\Delta\nu$ values. To arrive at a final analysis few characteristic progressions showing a decreasing interval and obeying the intensity criteria were selected and some of them are shown in plate (11).

Following the standard procedure (Herzberg 1950) for calculating the vibrational constants the band head equations given below were derived for the B - systems of the respective molecules. These quantum equations account in a satisfactory manner for most of the observed bands.

For CdCl :

$$\nu_{head} = 26010.1 + \left[153.5(v'+\tfrac{1}{2}) - 3.75(v'+\tfrac{1}{2})^2\right] - \left[330.4(v''+\tfrac{1}{2}) - 1.22(v''+\tfrac{1}{2})^2\right]$$

For CdBr :

$$\nu_{head} = 24822.6 + \left[105.4(v'+\tfrac{1}{2}) - 1.70(v'+\tfrac{1}{2})^2\right] - \left[229.9(v''+\tfrac{1}{2}) - 0.47(v''+\tfrac{1}{2})^2\right]$$

For CdI :

$$\nu_{head} = 24592.4 + \left[77.70(v'+\tfrac{1}{2}) - 1.45(v'+\tfrac{1}{2})^2\right] - \left[178.00(v''+\tfrac{1}{2}) - 0.60(v''+\tfrac{1}{2})^2\right]$$

When the bands of CdCl and CdBr molecules are arranged in their respective Deslandres' tables [Tables (5) and (14)] it is found that the intensity distributions bear a close resemblence to that observed in the corresponding halides of mercury. A preliminary spectroscopic study of the halides of the zinc in this laboratory, also showed the resemblance. The Condon parabolae for the B - systems of the cadmium halides appear to be sufficiently wide which probably account for the poor intensities of the bands having lower v' and v" values.

ISOTOPE EFFECT

Using the vibrational constants obtained for the molecule CdCl, the values of theisotopic shifts for (0, 12), (0,13) and (0, 14) bands were calculated. These values range between 75 and 85 cm^{-1} whereas the actual observed heads near these bands show a separation ranging between 15 to 35 cm^{-1}. Moreover the heads near (0, 14) and (0, 13) bands which one may think to be due to isotopic effect are not so sharp compared to that in front of (0, 12) band. This therefore indicates that these bands may not be isotopic heads of respective bands, but may probably be the members of the higher progressions and are therefore assigned accordingly.

As the two isotopes of bromine (Br^{79} and Br^{81}) occur in the ratio of 50.57 : 49.43 one may expect the intensities of the corresponding bands to be nearly the same. In the region $\lambda\lambda$4400-4700 A.U. (Plate 8) this isotopic effect gives the bands a double headed appearance. The isotopic shift for the vibrational band (v',v") is given by

$$\begin{aligned} \nu_{v_i} - \nu_v &= \Delta\nu \\ &= (\rho-1)\left[\omega_e'(v'+\tfrac{1}{2}) - \omega_e''(v''+\tfrac{1}{2})\right] - \\ &\quad (\rho^2-1)\left[\omega_e'x_e'(v'+\tfrac{1}{2})^2 - \omega_e''x_e''(v''+\tfrac{1}{2})^2\right] \end{aligned}$$

where ν_{vi} refer to $CdBr^{81}$ and ν_v to $CdBr^{79}$. The isotopic factors $(\rho-1)$ and (ρ^2-1) come out to be -0.00723 and -0.01443 respectively. Using these values the isotopic shifts for about ten bands were calculated. The observed separations were then compared with the calculated values. The agreement is quite close and is shown in table (15).

In the case of CdI bands isotopic effect is possible due to Cd atom only. However for the dispersion used this is not detectable and it may give rise to diffuseness of the band heads.

The systems analysed above are similar in all respects. Further since the lower states involved in these systems have the same frequencies as those of their respective ground states, it might be that these systems belong to a transition of the type $B^2\Sigma \rightarrow X^2\Sigma$. The possibility of a low lying $B^2\Sigma$ state for such molecules will be discussed in the next chapter.

(ii) Systems in red region (Plates - 5, 9 and 12).

Unlike the bands of the systems discussed above the bands in the red region for all these molecules are highly diffuse and appear to lie on two distinct continua. The bands in the case of CdI are somewhat more distinct than those of CdBr and CdCl. Further the intensity maxima of these molecules viz CdCl, CdBr and CdI move progressively towards the longer wavelength and the bands in the extreme red finally merge with a continuum.

Amongst the bands observed the spacing between the alternate members of bands ranged from 250 cm^{-1} to 276 cm^{-1} in the case of CdCl bands, from 155 cm^{-1} to 166 cm^{-1} in the case of CdBr bands while the spacing of 155 cm^{-1} to 142 cm^{-1} in the case of CdI is observed at an interval of two bands. A first attempt to arrange these bands in the vibrational scheme of their respective B - systems described above resulted in a failure. Further most of the bands between two intensity maxima appeared double headed. These evidences thus lead us to believe that a new state having a very low energy compared to that of B - state may exist for all the molecules. One of the pecularities which one may infer from the above is that the potential curves belonging to these states may have shallow minima. Because of the poor dispersion it is not possible to present a complete analysis. However the regularities of these bands are pointed out in tables 7, 17 and 24. Further an interval of about 1130 to 1140 cm^{-1}. between some of the intense bands of the two sub-groups lying on two different continua for all the molecules indicates a possibility of a low lying $^2\Pi$ state. That such a state exists theoretically will be discussed in detail in the next chapter.

(iii) Ultra-violet systems (plates - 2(a), (b) & (c)).

For all the molecules the C and D systems are degraded to shorter wavelength and have been assigned to a transition $^2\Pi \rightarrow {}^2\Sigma$ (Howell 1943).
Some additional information could be provided for C system of CdBr and is shown in table (12), the vibrational constants dervied from it are more reliable than those reported by earlier workers because more number of bands have been observed.

$\omega_e'' = 230 \cdot 00$ $\omega_e''x_e'' = 0 \cdot 50$

$\omega_e' = 254 \cdot 00$ $\omega_e'x_e' = 0 \cdot 50$

The detailed study of C and D systems of CdI with better dispersion is under plan.

(iv) As shown in plates 6(a) and 6(b) nearly thirteen bands in the case of CdBr and fourteen bands in the case of CdI are similar in appearance. They do not fit in the vibrational schemes of the systems of these molecules on the shorter wavelength side. They appear to be progression type and due to their limited number and crowded appearance an exact analysis is not possible. Still however from the view point of intervals and sudden change of intensity one can infer that they might be belonging to a different state. Their regularities have been shown in tables (9) and (19).

(v) The analysis of the bands of CdBr in the region $\lambda\lambda$2350-2550 A.U. (Plate 6(a)) and those of CdI in the region $\lambda\lambda$2360-2600 A.U. (Plate 10) have been given in tables (10) and (21). From the preliminary study of the analysis presented the lower state frequency comes out to about 208 cm^{-1} and the upper state frequency about 122 cm^{-1}. for CdBr molecule. In case the lower state involved in the emission of these bands is the ground state, the interval obtained is too low. However if the members observed belong to higher v" values such a value is possible. In case of CdI molecule unlike the previous workers the bands are sharp and accurate measurements were possible. Analysis of these bands have been reported by Howell (1943) and Ramasastry (1946), and both differ in certain respects. To facilitate the analysis the bands having sharp heads were picked up and were arranged in a progression (v'=0 as marked in plate (10).) The complete analysis was then followed up and vibrational scheme shown in table was prepared. The quantum equation given below was derived.

$$\nu_{head} = 42019{\cdot}48 + \left[107{\cdot}67\,(v'+\tfrac{1}{2}) - 1{\cdot}33\,(v'+\tfrac{1}{2})^2\right] - \left[178{\cdot}29\,(v''+\tfrac{1}{2}) - 0{\cdot}64\,(v''+\tfrac{1}{2})^2\right].$$

This accounts almost all bands in a satisfactory manner.

The analysis presented here will now be followed up in the next chapter considering electronic configuration and molecular states of halides of cadmium, and to compare them with the halides of the elements (Zn, Hg) of the same group as that of cadmium.