CHAPTER V

VIBRATIONAL ANALYSES

In this chapter are presented the vibrational analyses of the group of bands observed in the visible region for the molecules ZnCl, ZnBr and ZnI. These bands in the visible region may be assumed to arise due to two separate electronic transitions in each of the molecules. The nature of the bands observed for these molecules in the red region is different from the bands in the shorter wave length region. These two groups of bands are separated by a continuum (Plate 4) and in the beginning unsuccessful attempts were made to analyse all
these bands as due to one single electronic transition. The longer and shorter wave length groups of bands may be designated as systems A and B respectively. The vibrational analyses of the bands of ZnCl and ZnBr in the visible region have been carried out. In the case of ZnI the bands in the red region have been analysed and as the other group of bands are superposed by a general continuum accurate measurements were not possible. A regularity of interval exists amongst them and has been pointed out here. It is believed that the spectrum can be improved by studying the discharge spectrum in the atmosphere of argon and as soon as such facilities are available in the laboratory it is intended to take up the work again.

For the sake of convenience the analyses of the bands will be discussed in the following order:

(i) Vibrational analyses of the B-systems of ZnCl and ZnBr molecules.

(ii) Vibrational analyses of the A-systems of ZnCl, ZnBr and ZnI molecules.

B-SYSTEMS OF ZnCl AND ZnBr

The bands of ZnCl and ZnBr in this region are similar in their appearance. They also resemble to the
visible bands of CdCl and CdBr (Ramasastry, 1947; Patel and Patel, 1966 & 1967). The bands of ZnCl and ZnBr in the shorter wave length region are misleading as they show partial resolution of rotational structure. It was reported by Ramasastry that the rotational structure could be observed for the bands of CdCl even under the low dispersion of a constant deviation spectograph. It is very unlikely that a heavy molecule such as CdCl will show rotational structure under such a low dispersion and later, Patel and Patel suggested that they might be considered as vibrational bands. As the molecules ZnCl and ZnBr are also moderately heavy they cannot be expected to show open rotational structure under the dispersion used in the present investigation. The usual regularity in the spacing of the rotational lines could not be observed here. Moreover, the intervals between the so-called lines here are certainly more than what one can expect for the spacing between rotational lines of such heavy molecules under the medium dispersion used in the present study. It was found that these line-like structure observed in ZnCl and ZnBr could be satisfactorily accounted by assigning them the appropriate values of the vibrational quantum numbers.
A clue to the analysis of the bands of ZnCl was obtained from the sharp bands in the shorter wavelength region. Selecting some of the intense bands in this region, it was observed that the interval between successive band heads was unequal and varied from 157 to 176 cm\(^{-1}\). A regularly decreasing interval of about 348 to 328 cm\(^{-1}\) was found for alternate bands in the longer wavelength region. The ground state frequency observed for this molecule from the analysis of the near ultraviolet bands is 390.5 cm\(^{-1}\) (Cornell, 1938) and hence it was assumed that the bands observed here may be due to the higher vibrational quantum numbers.

At the outset of the analysis of ZnBr bands, attention was concentrated on the bands around 3800 Å where they are quite sharp. It was observed that for most of the halides of this group of the periodic table the intensity distribution follows an open Condon parabola. It is therefore suggestive that the bands in the region around 3800 Å may form the apex of the parabola. Careful measurements of the bands in this region revealed that a decreasing separation ranging from 270 cm\(^{-1}\) to 255 cm\(^{-1}\) amongst alternate members of this group exists.
The progressions marked on Plate 8 were first selected under this basis and a systematic analysis was then followed up.

The Condon parabolae observed for the band systems of ZnCl and ZnBr appear to be sufficiently wide, which may probably account for the poor intensities of the bands having lower vibrational quantum numbers.

All the bands observed for the two molecules could be well represented by the following vibrational quantum formulae.

For ZnCl:

\[ \nu_{\text{head}} = 27316.2 + \sqrt{185.9 (v'+\frac{1}{2})} - 0.53 (v'+\frac{1}{2})^2 - \sqrt{391.0 (v''+\frac{1}{2})} - 1.50 (v''+\frac{1}{2})^2 \]

For ZnBr:

\[ \nu_{\text{head}} = 25138.7 + \sqrt{135.8(v'+\frac{1}{2})} - 0.40 (v'+\frac{1}{2})^2 - \sqrt{269.8(v''+\frac{1}{2})} - 1.54 (v''+\frac{1}{2})^2 \]

With the above vibrational constants and the quantum number assignments confirmation of the schemes for ZnCl and ZnBr was sought with the help of the isotopic shifts due to their halogen atoms. The isotopic separations in the case of the less abundant molecules
ZnCl\textsuperscript{37} and ZnBr\textsuperscript{81} have been calculated using the formula:

$$\Delta \nu = (\rho-1) \left[ \omega_e' (\nu'+\frac{1}{2}) - \omega_e'' (\nu''+\frac{1}{2}) \right] - 
(\rho^2-1) \left[ \omega_e' \omega_e' (\nu'+\frac{1}{2})^2 - \omega_e'' \omega_e'' (\nu''+\frac{1}{2})^2 \right]$$

The shifts due to Cl\textsuperscript{35} and Cl\textsuperscript{37} were calculated for some of the intense bands and the isotopic factors $(\rho-1)$ and $(\rho^2-1)$ come out to be -0.0175 and -0.0346 respectively. In Table V are collected the observed and calculated isotopic shifts and the agreement is found to be quite close.

The two isotopes Br\textsuperscript{79} and Br\textsuperscript{81} have the natural abundance ratio 50.6 : 49.4 and hence one may expect the intensities of the corresponding isotopic bands to be nearly the same. The isotopic factors $(\rho-1)$ and $(\rho^2-1)$ in this case are -0.0055 and -0.0110 respectively and using these values, the separations for some of the intense bands have been calculated. They are listed in Table XI along with the observed separations and are found to be in close agreement. The separations for the bands in the longer wavelength region are less than 5 cm\textsuperscript{-1} which may perhaps account for the diffuse nature of the bands in that region.
The lower state frequency obtained from the analysis of the system of ZnCl is in proximity with the ground state frequency of the molecule derived from the analyses of the C and D systems. The system may be considered as due to an electronic transition $B^2\Sigma \rightarrow X^2\Sigma$. This will be discussed in more detail in the next chapter. In an analogous way the band system observed for ZnBr should also be ascribed to the transition $B^2\Sigma \rightarrow X^2\Sigma$. However, the vibrational constants derived from the analysis for the lower electronic state agree neither with the constants for the ground state proposed by Howell (1943) nor with the values suggested by Ramasastry and Sreeramamurty (1950) from the analyses of the C and D systems of the molecule. Analysing the bands reported by Walter and Barratt (1928) in absorption, Howell suggested a value of $\omega_0 = 220 \text{ cm}^{-1}$ for the ground state of ZnBr molecule. Since this value is of the same order of magnitude as that of the ground state vibrational frequency of ZnI, Howell doubted the data attributed to ZnBr. Ramasastry and Sreeramamurty suggested a value of 312 cm$^{-1}$ and 318 cm$^{-1}$ respectively as the ground state frequencies for the two component systems of the $^2\Pi \rightarrow ^2\Sigma$ electronic
transition. The following points will, however, support the present analysis and the values of the vibrational constants derived from it.

(1) The analysis of the bands observed for this molecule in the red region is presented in the next section. It gives a value of $\omega_e = 266 \text{ cm}^{-1}$ for the lower state involved in the transition which is in good agreement with the value obtained for this system.

(2) An interval among the intense bands having the magnitude $315 \text{ cm}^{-1}$ is not observed anywhere in the system and apparently Ramasastry and Sreerammurthy could not analyse the bands they observed in this region. They, however, noticed that the bands are located at approximately equal interval of $130 \text{ cm}^{-1}$.

(3) From the analyses of the various band systems of ZnCl and ZnI it is known that their ground state vibrational frequencies are of the order of $390 \text{ cm}^{-1}$ and $223 \text{ cm}^{-1}$ respectively. The ground state frequency of ZnBr should then be expected to lie between these two values. The value obtained from the proposed analysis ($\omega_e = 269.8 \text{ cm}^{-1}$) satisfies this criterion.
(4) Ramasastry and Sreeramamurty had suggested that the $\omega_c^0$ value of ZnBr should lie between those of CuBr ($\omega_c^0 = 314$ cm$^{-1}$) and GaBr ($\omega_c^0 = 263$ cm$^{-1}$). The value of $\omega_c^0$ ($= 315$ cm$^{-1}$) suggested by them for ZnBr is, however, almost equal to the ground state frequency 314 cm$^{-1}$ of CuBr molecule while the value of $\omega_c^0$ derived from the present analysis is more consistent with this argument.

(5) The fact that the observed and calculated isotopic shifts are in good agreement gives an additional support to the proposed analysis.

(6) The near ultraviolet spectrum of the molecule is photographed at a dispersion of 3.6 A°/mm and a reproduction of it is given (vide Appendix). An interval of the order of 260 - 270 cm$^{-1}$ is possible amongst them and the details are given in the Appendix.

Owing to the weak intensity of the bands of zinc iodide in the region 4000 - 4650 A° and a general continuum covering them up, there is not much of contrast and consequently accurate measurements were not possible with the spectrograms obtained. Hence a conclusive analysis was not possible. However, an
interval ranging from 195 to 213 cm\textsuperscript{-1}, which is of the same order of magnitude of the ground state frequency of ZnI (\(\omega_0 = 223.4\) cm\textsuperscript{-1}), was found to exist among some of the bands. For example, the bands at 24235 cm\textsuperscript{-1}, 24036 cm\textsuperscript{-1}, 23833 cm\textsuperscript{-1} and 23629 cm\textsuperscript{-1} show intervals ranging from 199 to 204 cm\textsuperscript{-1}. All these are displayed in Plate 10.

**A-SYSTEMS OF ZnCl, ZnBr AND ZnI**

To begin with the analysis of the ZnCl bands in the red region the bands in the shorter wavelength part were picked up as the banded structure is more distinct there. No regularity in the interval was observed between successive bands in this region. However, a uniform increase in the interval ranging between 100 and 110 cm\textsuperscript{-1} was noticed at 5553.9 Å, 5585.2 Å, 5618.0 Å and 5651.6 Å and attempts to arrange them in a progression were not successful. Hence they were considered to form a sequence. These bands show definite band structure and mere such sequences could be selected from the group of bands observed.

Although the bands observed for ZnBr and ZnI are free from the secondary spectrum of hydrogen a
great deal of difficulty was experienced in analysing them because of the crowded appearance of the bands and the general continuum covering them up. In the case of ZnBr the bands in the region 5800 – 6000 Å are comparatively sharp and also intense. A search to find out an interval of either 315 cm\(^{-1}\) or 270 cm\(^{-1}\) was made among them. The interval having the magnitude 270 cm\(^{-1}\) was noticed among some of the bands while no interval of 315 cm\(^{-1}\) was found feasible. The intense bands at 5930.5 Å, 5951.8 Å and 5972.9 Å appear to form a sequence with a wave number interval approximately equal to 60 cm\(^{-1}\). More such sequences could be picked up from the group of bands and the analysis was followed up.

The bands of ZnI in the red region resemble in their appearance to those of ZnBr molecule. The most intense and sharp bands of ZnI are in the region 5990 – 6050 Å. The starting point of the analysis was the set of bands beginning at 6040 Å and extending towards shorter wave lengths. These bands are found to form sequences. For example, the intense bands at 6040.0 Å, 6018.0 Å, 5996.5 Å and 5977.1 Å.
form a sequence. The bands at 6033.2 Å*, 6012.5 Å* and 5991.7 Å* may form another sequence.

It was found that the bands observed in the red region for ZnCl, ZnBr and ZnI could not be accounted in a single system. The existence of a low-lying $^2\Pi$ state in the molecules is known and in all probability the bands observed here in each molecule may be due to an electronic transition involving $^2\Pi$ as one of the states. Hence the bands observed in the red region may be ascribed to a transition $A^2\Pi - X^2\Sigma$. The following are the doublet intervals observed in the present analyses of the three diatomic molecules.

$$
\begin{align*}
ZnCl & : 396.0 \text{ cm}^{-1} \\
ZnBr & : 419.5 \text{ cm}^{-1} \\
ZnI & : 398.0 \text{ cm}^{-1}
\end{align*}
$$

It may be mentioned here that the analysis suggested for ZnCl is only tentative and could not be improved further because of the presence of the impurity spectrum of hydrogen.

All the main band heads of the three molecules can fairly well be represented by their respective
vibrational quantum equations derived from the
vibrational analyses.

For ZnCl:
\[ \lambda_{\text{head}} = 17757.7 \} + \sqrt{297.5 \left( v^1 + \frac{1}{2} \right)} - 3.09 \left( v^1 + \frac{1}{2} \right)^2 \]
\[ - \sqrt{390.1 \left( v^n + \frac{1}{2} \right)} - 1.53 \left( v^n + \frac{1}{2} \right)^2 \]

For ZnBr:
(i) \[ \lambda_{\text{head}} = 16887.8 + \sqrt{203.8 \left( v^1 + \frac{1}{2} \right)} - 0.55 \left( v^1 + \frac{1}{2} \right)^2 \]
\[ - \sqrt{266.0 \left( v^n + \frac{1}{2} \right)} - 1.80 \left( v^n + \frac{1}{2} \right)^2 \]
(ii) \[ \lambda_{\text{head}} = 17307.3 + \sqrt{204.3 \left( v^1 + \frac{1}{2} \right)} - 0.50 \left( v^1 + \frac{1}{2} \right)^2 \]
\[ - \sqrt{265.7 \left( v^n + \frac{1}{2} \right)} - 1.75 \left( v^n + \frac{1}{2} \right)^2 \]

For ZnI:
(i) \[ \lambda_{\text{head}} = 17835.2 + \sqrt{156.5 \left( v^1 + \frac{1}{2} \right)} - 0.55 \left( v^1 + \frac{1}{2} \right)^2 \]
\[ - \sqrt{223.6 \left( v^n + \frac{1}{2} \right)} - 0.80 \left( v^n + \frac{1}{2} \right)^2 \]
(ii) \[ \lambda_{\text{head}} = 18233.2 + \sqrt{153.7 \left( v^1 + \frac{1}{2} \right)} - 0.55 \left( v^1 + \frac{1}{2} \right)^2 \]
\[ - \sqrt{222.2 \left( v^n + \frac{1}{2} \right)} - 0.80 \left( v^n + \frac{1}{2} \right)^2 \]