SUMMARY

The thesis embodies a detailed and systematic vibrational analyses of the emission spectra of the halides of zinc in the visible region. A high-frequency oscillatory discharge is found to be the most suitable and convenient source for the excitation of the molecules so as to get their spectra in the visible and ultraviolet regions. The spectra were photographed on three spectrographs, each having different dispersions. A preliminary survey on the band spectra of zinc chloride, zinc bromide and zinc iodide is made with Hilger medium quartz and E2 glass spectrographs. Whenever higher dispersion was found desirable the spectra were obtained on a Carl-Zeiss plane grating spectrograph which has a dispersion of 7.3 Å/mm at the first order.

The thesis has been divided into two parts. An introduction to the thesis, the experimental techniques employed and the historical survey of the problem are given in Part I. In order to make the thesis self-contained a brief description of the theory of band spectra is given. The sources which are generally employed to study the emission spectra of diatomic
molecules are also elucidated. The high-frequency electrodeless discharge is described in detail as it served to excite the spectra of the molecules reported here.

The results obtained on the band systems of the diatomic spectra of the halides of zinc in emission as well as their vibrational analyses are discussed in detail in the Part II. The molecules zinc chloride, zinc bromide and zinc iodide show extensive band systems from visible to ultraviolet. The ultraviolet bands of the molecules were subjected to detailed study by earlier workers, whereas the bands in the visible region were practically unexplored. All the bands in the visible in each molecule were hitherto assumed as due to one single electronic transition. However, the present study revealed that they arise due to two separate electronic transitions and are designated as systems A and B. The low-lying state A in these molecules is shown to be a $^2\Pi$ state and the group of bands observed in the red region is ascribed to a $^2\Pi - ^2\Sigma$ transition. The next excited state in zinc halide molecules is known to be $^2\Sigma^+$, and hence the bands obtained in the lower part of the visible region may be due to a transition $B^2\Sigma - X^2\Sigma$. 
The B-systems of ZnCl and ZnBr molecules occur in the region 4700 - 3800 Å and 4550 - 3600 Å respectively. They are analysed and the vibrational quantum formulae have been derived. The vibrational isotope effect due to Cl\textsuperscript{37} in the zinc chloride bands and that due to Br\textsuperscript{81} in the zinc bromide bands have also been established. However, the vibrational frequencies of the ground state of the ZnBr molecule derived from the present analysis do not agree with the constants proposed by the earlier workers. The reasons in favour of the constants derived from the present analysis have been elucidated. The ZnI molecule also shows a corresponding group of bands in the region 4650 - 4000 Å and as they are overlapped by a strong continuum the vibrational analysis could not be carried out. A regularity of interval having the order of magnitude of the ground state vibrational frequency of the molecule has been obtained.

The other group of bands in the red region observed for zinc chloride, zinc bromide and zinc iodide show degradation towards red and have crowded appearance. The vibrational analyses for these bands have been carried out for the three halides of zinc and for each of them the vibrational quantum formula
has been derived which represents in a satisfactory manner all the observed band heads. From the analyses a $^2Π$ interval of about 400 cm$^{-1}$ is obtained for all the three molecules.

The electron configurations of the ground state as well as the two low-lying excited states are given in Chapter VI. A comparison of the vibrational frequencies in the ground state of the halides of zinc is made with those of Cu and Ga. The electronic states of chlorides, bromides and iodides of zinc are compared with those of cadmium and mercury as the three metal atoms belong to the same group in the periodic table and are expected to show similar spectroscopic properties. The dissociation energies for the ground states of the three molecules have been calculated and are presented in Chapter VII.

The near ultraviolet bands of ZnI and ZnBr have been obtained on the grating spectrograph and are shown in Appendix. Twelve additional bands belonging to the C-system of ZnI have been obtained. A tentative vibrational scheme is proposed for the C and D systems of ZnBr molecule with a ground state frequency of the order of 270 cm$^{-1}$. 