

SUMMARY

The thesis embodies a detailed and systematic analyses of the ultraviolet emission spectra of the halides of mercury. A high frequency discharge source was found to be the most suitable to excite the molecules. In order to carry out a preliminary survey of the various band systems associated with mercury chloride, mercury bromide and mercury iodide, a Hilger medium quartz spectrograph was employed. Having established the conditions of excitation, the spectra were recorded on a Carl-Zeiss plane grating spectrograph at a dispersion of $1.85 \text{ \AA}^\circ/\text{mm}$. and a detailed study was carried out.

The thesis is divided into two parts. Part I includes an introduction to the subject, historical survey of the work reported earlier on the spectra of the molecules under consideration and the experimental techniques employed to obtain the spectra. In order to make the thesis self-contained, a brief account of the vibrational structure of the bands and intensity distribution in a band system are given. The main object in selecting the molecules is also elucidated. The sources which are generally employed in the study of the spectra of diatomic molecules ^{are} discussed. The high frequency electrodeless discharge source is described in detail as it served to excite the spectra of molecules reported here.

The results obtained in the present study and the analyses of the various band systems carried out on the spectra of diatomic molecules of mercury chloride, mercury bromide and mercury iodide are included in Part II. The electron configurations of the various electronic states involved in the band systems selected for the present study are discussed in detail. The conclusions drawn from the study are also presented.

Though the spectra of halides of mercury in the ultraviolet are known since long, it was not found possible to establish the correct order of the doublet interval of the upper $^2\Pi$ state involved in the production of C and D systems. The doublet interval of the $^2\Pi$ state is related to the 3P width of the mercury atom and the present analyses showed good agreement between the observed and theoretically calculated values for all the halides of mercury. This interval, in addition, is inkeeping with the $^2\Pi$ intervals known for the halides of zinc and cadmium.

The analyses of the E systems of mercury bromide and mercury iodide have been revised. The E system of HgI molecule is attributed to an electronic transition $^2\Sigma - ^2\Sigma$ in the present work. Further, a group of double-headed bands of HgBr is reinvestigated and a $^2\Sigma - ^2\Sigma$ transition is

suggested for it. For the first time, rotational structure of some of the bands of the D system of HgCl molecule is observed and a preliminary rotational analysis is carried out and the rotational constants are derived. The vibrational and rotational constants obtained from the present study are also reported. As the elements Zn, Cd and Hg belong to the same group of the periodic table, they are expected to have similar spectroscopic properties and hence a comparison of their vibrational frequencies is made. The various electronic states of the halides of mercury are correlated with those for the halides of zinc and cadmium.

The thesis has been appended by the results and analyses of the band spectra of CdI molecule to verify and support the results and conclusions drawn therefrom for the ultraviolet spectra of the halides of mercury.