Chapter - V

SUMMARY & CONCLUSIONS

5.1 Force Constant and Electronegativities:

The force constant gives information regarding the nature of bonding in the molecule. The interpretation of force constant in terms of electronegativities is very important. Three different new relations are suggested for force constant which are of the form -

1) $k_e = a (r_e - d)^{-3}$

with $d = c \left[r_e - \dfrac{r_e^{\frac{1}{2}}}{(e_1 e_2)^{\frac{1}{4}}} \right]$

where, a and c are the constants for a group of molecules.

2) $k_e = PX^2 + QX + R$

where, P, Q and R are the constants for a group of molecule

and $x = \dfrac{(Ne_1 e_2)^{\frac{1}{2}}}{r_e}$.

3) $\log k_e = BX + A$

where, A and B are the constants for the same type of molecules.

Using these relations, force constants are computed for a number of diatomic molecules. It is observed that the values of force constant obtained using these relations are better as compared to those obtained by using Gordy's relation.

Using these relations, we have computed the values

of anharmonicity constant ($\omega_e x_e$) and the zero point mean square amplitude $\langle (r-r_e) \rangle$. We have observed that the values of these parameters computed using the new relations are closer to experimental values than those obtained by using Gordy's relaton. Hence, we found that the applicability of the proposed relations is satisfactory.

There are different methods suggested for the computation of bond order.[2,3] We have calculated bond order using the concept of covalence force. Using this bond order, we have obtained the values of zero point mean square amplitude of vibration and force constant. It is observed that the values are in close agreement with the experimental values.

5.2 Potential Energy Function for a Diatomic Molecule.

Potential energy function gives good deal of information regarding the structure of molecule. It is very important to represent correctly the potential energy curve by using suitable function. There are different forms to represent potential energy function.[4] The Morse Function[5] is widely employed as it provides convenient analytical expression for the potential.But it cannot represent adequately many an electronic state. Hence, it is necessary to construct a true potential energy curve fitting out the classical turning points. Vaidyan and Santaram[6-8] suggested a rapid method for the construction of true potential energy curve. This method has been applied for the states B and X of XeF, $A^2\Delta_{5/2}$, $B^2\Delta_{5/2}$ and
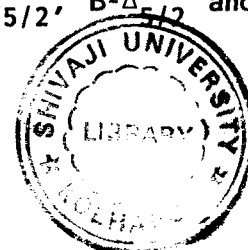
$X^2\Delta_{5/2}$ states of PtH and PtD, $X^2\Sigma$ and $A^2\Pi_{3/2}$ states of YbF, A and X states of HoF, X of SiTe and LuF, $A^3\Pi_0^+$, $B^2\Pi_1^+$ and $X^1\Sigma^+$ of InBr. It is observed that the turning points obtained are in agreement with RKRV data.

Using Lakshman and Rao[9] method, the classical turning points are computed for the states B and X of XeF, $A^2\Delta_{5/2}$, $B^2\Delta_{5/2}$ and $X^2\Delta_{5/2}$ of PtH and PtD. The turning points obtained by this method are found to give good agreement with experimental values.

A new functional relation is sggested[10] for those states where the graph of $\log[\omega_e \pm (4\omega_e x_e U)^{\frac{1}{2}}]$ versus r deviate considerably from the straight line. The functional relation for the diatomic molecular potential is of the form.

$$f(U) = \gamma r^2 + \rho r + c.$$

The constants involved in the expression are computed by least square procedure. This functional formula is applied to compute classical turning points of the states B and X of XeF, $A^2\Delta_{5/2}$, $B^2\Delta_{5/2}$ and $X^2\Delta_{5/2}$ of PtH and PtD, $X^2\Sigma$ and $A^2\Pi_{3/2}$ of YbF, A and X of HoF, X of SiTe and LuF and $A^3\Pi_0^+$, $B^2\Pi_1^+$ and $X^1\Sigma^+$ of InBr. The turning points are found in close agreement with RKRV data.

5.3 Franck-Condon Factors and r-Centroids.

Using three different methods, namely, Bate's Method,[11,12] Manneback Method,[13,14] & Fraser-Jarmain Method[15,16] Franck-Condon

factors were computed for the band systems $A'\Pi\text{-}X'\Sigma^+$ and $B'\Sigma^+\text{-}X'\Sigma^+$ of CuF, $E^2\Delta_{5/2}\text{-}X^2_2\Pi_{1/2}$ of CuO, $A^2\Sigma^+\text{-}X^2\Pi_i$ of CuSe, A-X of CuTe, $A^2\Sigma^+\text{-}X^2\Sigma^+$ of AlSe, $d'\Sigma^+\text{-}C'\Pi$ and $d'\Sigma^+\text{-}b'\Sigma^+$ of NH, $d'\Sigma^+\text{-}C'\Pi$ of ND, $A'\Pi\text{-}X'\Sigma^+$ of PN, $A^2\Pi_0^+\text{-}X'\Sigma^+$ and $B^3\Pi_i\text{-}X'\Sigma^+$ of InBr. The F.C. factors obtained by using Bate's method and Manneback's method are found in agreement with those obtained by using Fraser-Jarmain method.

The r-centroids are calculated by using Nicholls and Jarmain[17] graphical method. The r-centroids are computed for the band systems of $A'\Pi\text{-}X'\Sigma^+$ and $B'\Sigma^+\text{-}X'\Sigma^+$ of CuF, $A^2\Sigma^+\text{-}X^2\Pi_i$ of CuSe, A-X of CuTe, $A^2\Sigma^+\text{-}X'\Sigma^+$ of AlSe, B-X of XeF, $A^2\Pi_0^+\text{-}X'\Sigma^+$ and $B^3\Pi\text{-}X'\Sigma^+$ of InBr. The functional relation is used to compute r-centroids of the band system B-X of XeF, $A^2\Pi_0^+\text{-}X'\Sigma^+$ and $B^3\Pi_i\text{-}X'\Sigma^+$ of InBr. The r-centroids are found to vary directly or inversely with wavelength depending on $(r'_e\text{-}r''_e)$ in positive or negative. The r-centroids obained by using functional formula are found to be different from those obtained by using Morse function. This differnce must be due to deviation from Morse function.

In conclusion, the following points emerge from the present work:

1) Our relations for force constant in terms of electronegativity and internuclear distance are quite satisfactory in producing reliable data on force constants (k_e),zeropoint mean square amplitude $(r\text{-}r_e)$, anharmonicity constant $(\omega_e x_e)$ for a large number of diatomics.

2) The method for the calculation of bond order is being tested for computation of force constants in large number of diatomics. The bond order calculated by using this new approach has resulted in giving better data on force constants.

3) (a) New functional relations proposed in the present work are useful for constructing P.E. curves in the case of molecules where Morse potential is inadequate.

(b) Extended Rydberg potential is used to compute potential energies in HoF and YbF molecules.

4) Franck-Condon factors are computed using Fraser and Jarmain method, Manneback's method and Bate's method. It is observed that the values obtained by using Manneback method and Bate's method are comparable with Fraser and Jarmain method.

5) r-centroids are obtained using graphical method and using functional relation. The values obtained using functional relation are different from those obtained by using Morse function. This is because of the deviation from Morse function.

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