

PREFACE

In this Dissertation are presented the theoretical investigations made by the author on the problems of the determination of potential energy curves and calculations of spectroscopic constants for a number of non-polar and polar diatomic molecules. The Dissertation comprises five chapters.

The Chapter 1 deals with potential energy curve and methods to determine the same. In the beginning the basic concepts leading to the formation of a potential energy curve have been briefly explained. The description and importance of such a curve are subsequently given. Next the general methods for the determination of potential curves have been described in detail. Particularly, a few modified versions of RKR method are dealt with at length. The details regarding some of the important semiempirical functions used for reproducing the P.E. curves are also outlined. Finally the various types of ionic potential functions applicable to the polar molecules are discussed in detail.

The calculations of spectroscopic constants and the study of variation of Varshni's functions F & G with Sutherland's parameter (Δ) by a newly suggested Generalized Combination Potential (GCP) form the subject matter of Chapter 2. At the outset it has been noted that the combination potentials involving Rydberg potential are found to be more successful in the determination of potential energy curves and spectroscopic constants for non-polar diatomic molecules. This has instigated a need for modifying the constituent functions in the combination potentials involving Morse function. In the present work a Generalized Combination Potential (GCP) is proposed as given below :

(ii)

$$U(\rho) = D_e \left[1 - \exp(-b\rho) + \rho^3 \exp(-b\rho) F(\rho) \right]$$

with $F(\rho) = (n + b\rho) \exp(-b\rho)$ and

$$\rho = (r - r_e)/r_e$$

The salient features of this newly suggested potential is that it involves a function $F(\rho)$ which takes variety of values depending on the parameter n so as to satisfy the necessary criteria $U(0)=0$ and $U(\infty) = D_e$. The Hulbert-Hirschfelder function is found to be a special case of the GCP function. By varying n , one can find its best values which give maximum accurate results for different groups of molecules.

Expressions for the spectroscopic constants α_e and $\omega_e x_e$ are derived by the well known Varshni's method. These are applied to a number of non-polar diatomic molecules. The calculated results show that the GCP function evaluates most accurate α_e and $\omega_e x_e$ constants for different groups of molecules formed according to best n values. Further, the GCP function with $n=0$ gives F values in good agreement with experimental results. However, these are found to be greater than the corresponding values on Morse and Rydberg functions, thereby voilating Varshni's criterion. Nevertheless we conclude that the accuracy of F values should also be simultaneously considered in deciding the validity of potential function on the basis of Varshni's conclusions. The variation of F and G versus Δ on GCP is in reasonably good agreement with the

(iii)

experimental straight line curves.

In Chapter 3 we have given the calculations of RKR potential energy curves for non-polar diatomic molecules using the GMR function which is a special case of GCP function proposed in the earlier chapter. In the beginning the salient features of RKR procedure are given. The various criteria to determine the best fit among the empirical and true potential curves by this method have also been studied. Next the detailed results of the RKR calculations using GMR function have been presented both graphically and intabular form. For a comparative study, the RKR curves using Morse and Rydberg functions are also given. The modified RKR method due to Reddy and Reddy[†] has been employed along with suitable computer programs for a rapid and accurate computations of the results. Among the different diatomic molecules chosen for this study we have obtained the dissociation energies for AgCl, AgH and Br₂ molecules which are partly ionic and partly covalent in nature. The reproducibility of the potential energy curves for these molecules show that the GMR function can be successfully used in the case of molecules belonging to this category. The potential energy curve calculations for the excited state of some molecules have also been given at the end of this chapter.

At the outset of Chapter 4, we have brought out the importance of binding energy of ionic molecules in many problems

[†] Reddy R.R. and Reddy A.S.R., Ind. J. Phys. **59B**, 13 (1985)

(iv)

of scientific research. We have taken a literature survey of a number of ionic potential functions which are applied mainly to calculate the binding energies of alkali halides and hydrides and heavy metal halide molecules. This study shows that the repulsive terms used in the various ionic potential functions involve both integral and half integral powers of the internuclear distance (r) in the exponential and its multiplying coefficients. There is not a single potential which can be successfully applied to all the types of ionic molecules mentioned above. Most of the calculations using these potentials are reported on old data of the molecular constants r_e , k_e and D_i .

In view of the above said observations we have formulated two new potential energy functions of the most generalized forms so as to improve the accuracy of binding energy calculations with the help of recent molecular data.

Generalized Logarithmic Potential (GLP)

$$U(r) = \left(-\frac{e^2}{r} \right) + G \ln \left[2^{n-1} + \left(\frac{H}{r^{4/n}} \right) \right]$$

where G and H are the potential parameters. It is interesting to note that by putting $n=1$ and 2 we obtain the logarithmic potentials (1) and (2) respectively due to Thakur et al.*

By the usual procedure the expression for the binding energy comes out to be

* Thakur K.P. and Pandey J.D., Chem.Phys. **71**, (1974) 850.

(v)

$$D_i = (e^2/r_e) \left[1 - (n(1-P)/4) \ln \left[2^{n-1}(1-1/P) \right] \right]$$

where

$$P = \frac{(k_e r_e + e^2/r_e^2)}{(k_e r_e + e^2/r_e^2) - 4e^2/n r_e^2}$$

Generalized Exponential Potential (GEP)

$$U(r) = (-e^2/r) + P r^n \exp(\pm r^m/Q)$$

where P and Q are the potential parameters and n takes positive or negative integral values while m can take both positive and negative integral as well as fractional values. For suitable combinations of n and m values and the proper sign of the exponent, we can obtain different exponential types of potentials available in the literature e.g.

- i) For $n=0$, $m=1$ and negative sign in the exponent we obtain Born-Mayer potential.
- ii) For $n=0$, $m=1.5$ and positive sign in the exponent we get modified Gaussian potential.

On GEP potential we have obtained the following expressions for the binding energy.

$$D_i = (e^2/r_e) \left[1 + \frac{1}{(n + m r_e^m / Q_1)} \right]$$

and

$$D_i = (e^2/r_e) \left[1 + \frac{1}{(n - m r_e^m / Q_1)} \right]$$

where Q_1 and Q_2 are the values of potential parameter Q obtained as the roots of quadratic equation.

Next we have presented the binding energy calculations of a number of ionic molecules using both GEP and GLP functions for different combinations of the parameter values involved in them. The calculations show that, in general the logarithmic type of potentials (especially GLP function with $n=3$) are more successful in the case of alkali halides as compared with exponential type of potentials. However, in the case of alkali hydrides these potentials yield poor results. Regarding heavy metal halides it is found that GLP function with $n = 6$ and 7 evaluates most accurate binding energies. About the performance of GEP function it has been observed that with $n = 6$ and $m = 2$, this function is found to be most satisfactory for alkali halide molecules. This function with $n=0$ and $m=2$ is also found to give best results for alkali hydrides. However, the function is not at all suitable in the evaluation of the binding energies of heavy metal halides.

In the last Chapter of this Dissertation we have presented the estimates of spectroscopic constants of polar diatomic molecules on GEP and GLP functions proposed in Chapter 4. In the beginning the expressions for potential parameters of the two types of functions have been derived. Also the expressions for α_e , $\omega_e x_e$ and higher order spectroscopic constants are reported in each case. Computer programs developed for a rapid evaluation are also given in various Tables. In the case of alkali halides and hydrides the GEP function with $n=0$ and $m=1$ gives satisfactory results while GLP

(vii)

function with $n=1$ is not at all satisfactory. For heavy metal halides the GEP function with $n=2$ and $m=2$ gives satisfactory results as against very high percentage error calculated on GLP function. These observations are more or less true also for the calculations of $\omega_e x_e$ constants. Our calculations of higher order spectroscopic constants for various ionic molecules may be first of their kind because the relevant reliable experimental data are not available to our knowledge,