CHAPTER IV
POTENTIAL ENERGY CURVES

4.1 Potential energy curves

The potential experienced by the nuclei in a diatomic molecule varies as a square of \((r-r_e)\), where \(r_e\) is an equilibrium internuclear distance. To the first approximation the curve between potential energy and \(r\) is the parabola. The dependence of potential energy on higher orders of \((r - r_e)\) i.e. cubic, quartic etc. makes the potential anharmonic and therefore the potential energy curve deviates from the harmonic oscillator for higher vibrational levels. At higher \(r\) values the potential energy is asymptotically parallel to \(r\) axis called the dissociation energy \((D_e)\) of the molecule if measured from the minima of the potential energy curve. At low \(r\) values the potential energy tends to very high values and at \(r = r_e\) the potential energy is zero. There is no minima in the PE curves for the repulsive states.

For each vibrational level \(v\), the potential energy is \(G(v)\) and the points on the PE curve are \(r_{\text{min}}\) and \(r_{\text{max}}\) (or \(r_-\) and \(r_+\)) are called turning points. As \(v\) increase \(| r_+ - r_- |\) also increases. The separation between consecutive vibrational levels \(\Delta G_{v+1/2}\) also goes on decreasing with increasing \(v\) for an anharmonic oscillator [11].
4.2 Rydberg Klien Rees curves

The method of drawing potential energy curves (PE curves) based on the spectroscopic constant like $\omega_e$, $\omega_e x_e$, $B_e$, $\alpha_e$, $r_e$ etc. was developed by Rydberg, Klien and Rees [15-18]. Further it was modified by Vanderslice [19, 20]. There are various computer programmes developed but the recently developed one is that of Le Roy [82]. A brief account of RKR calculation is also given by Castano et al. [83]. The programme developed by Castano et al. is used in present work for the computations of RKR curves. Prior to this it was tested for CO and I$_2$ molecules. CO has probably deepest potential well, as the dissociation energy is 90543 cm$^{-1}$. Using the molecular constants of Farrenque [84] the RKR curve up to $v = 75$ was constructed where the PE is 90260 cm$^{-1}$. Another molecule is I$_2$ whose $D_e$ is 12547 cm$^{-1}$. The RKR curve was computed up to $v = 76^{th}$ level, where PE is 11700 cm$^{-1}$. The $r_{\text{min}}$, $r_{\text{max}}$ values in this case differ from Castano by 0.0009 Å only for highest vibrational level.

4.3 RKR calculations of different states of InCl

The turning points of $X^1\Sigma^+$, $A^3\Pi_0$, and $B^3\Pi_1$ are computed and RKR curves are constructed. The curves are shown in Fig. 4.1, Fig. 4.14, and Fig 4.15 respectively and their energies and turning points are shown in Table 4.3(b), 4.8, and 4.9 respectively.
4.4 Empirical potential energy functions

There are several mathematical expressions of potential energy functions known as empirical potential energy functions, which use to molecular constants derived from spectroscopic analysis. Few of them are Morse [85], Rydberg [15] Hulbert – Hirschfelder [86], extended Rydberg [87, 88] and Zavitsas [89] potential functions.

A survey of various potential functions is taken by Varshni [21], Goodisman [90], Bharate [22], Birajdar [23] and Shelke [40].

In the present study, it is decided to use the Hulber- Hirschfelder, Extended Rydberg and Zvitsas potential energy functions and to compare them with RKR Potential energy curves.

4.4.1 The H – H potential function

This function is defined as follows.

\[ U_{H-H}(r) = D_e \{[1- \exp (-a (r- r_e))]^2 + cx^3 (1+ bx) \exp (- 2x) \} \]  \quad ...  \quad (4.1)

where \( D_e \) is dissociation energy

\[ a = \frac{\omega_e}{[2(B_e D_e)^{1/2} r_e]} \]  \quad ...  \quad (4.2)

\[ c = 1+ a_1 (D_e/a_0)^2 \]  \quad ...  \quad (4.3)

\[ b = 2 - \{[(7/12) - (D_e \cdot a_2)/a_0] / c \} \]  \quad ...  \quad (4.4)

\[ a_0 = \frac{\omega_e^2}{4B_e} \]  \quad ...  \quad (4.5)

\[ a_1 = -1 - [\omega_e \alpha_e/6B_e^2] \]  \quad ...  \quad (4.6)

\[ a_2 = [5/4]a_1^2 - [2/3][\omega_e x_e / B_e] \]  \quad ...  \quad (4.7)

All constants have their usual meanings. \( a_0, a_1, \) and \( a_2 \) are known as Dunham coefficients.
4.4.2 The extended Rydberg potential function

In 1982 Huxley and Murrell [88] reported a potential function so as to build up a database. The function is similar to that of Rydberg [15] and that is why it is known as an extended Rydberg potential function. It has a form,

\[ U_R(r) = D_e - D_e \{ 1 + a_1 \rho + a_2 \rho^2 + a_3 \rho^3 \} e^{-\rho/a_1} \] \hspace{1cm} (4.8)

Where \[ \rho = r - r_e \] and \[ a_1, a_2, a_3 \] are constants \hspace{1cm} (4.9)

The function is an excellent representation of ground state potential for the stable diatomic molecules in their valence region, which contains attractive well, except for the long range Van der Waal region for which this equation does not have correct asymptotic form. In fact this potential function was investigated by Murrell and Sorbie [87] and Huxley and Murrell [88] after studying the large number of functions including the Hulbert-Hirschfelder (H-H) potential function.

Here \[ D_e \] is expressed in conventional form, viz

\[ D_e = D^0_0 - (1/2) \omega_e + (1/4) \omega_e x_e + E_{at} \] \hspace{1cm} (4.10)

Where \[ E_{at} \] is the energy of atoms on dissociation, relative to their ground states. The force – field parameters are

\[ f_2 = 4\pi^2 m \omega_e^2 c^2 \] \hspace{1cm} (4.11)

\[ f_3 = (3f_2/r_e)[1+(\alpha_c \omega_e 6B_c^2)] \] \hspace{1cm} (4.12)

\[ f_4 = (f_3/r_e^2)[15[1+(\alpha_c \omega_e 6B_c^2)] - 8 \omega_e x_c B_c}] \] \hspace{1cm} (4.13)

Where \[ f_n \] are the \[ n^{th} \] derivative of the potential at the equilibrium distance \[ r_e \].

The method of calculating \[ a_1 \] in equation is as follows,
The first step is to solve the following quartic equation for $a_1$

$$D_e a_1^4 - 6f_2 a_1^2 - 4f_3 a_1 - f_4 = 0$$ … (4.14)

If the roots are real, then since $f_4$ is always positive there must be one or three positive roots of equation (4.14). For acceptable equation the largest positive root gives the best result. Once $a_1$ is known then all other parameters can be calculated.

By differentiating equation (4.14) we get,

$$a_2 = (1/2) [a_1^2 - (f_2/D_e)]$$ … (4.15)

$$a_3 = a_1 a_2 - (a_1^3 / 3) - (f_3 / 6D_e)$$ … (4.16)

In some cases, it was observed by Huxley and Murell [88] that the solution of equation (4.14) has one $+$ve, one $-$ve and a pair of complex conjugate roots whose real part is largest than the real $+$ve root and whose imaginary part is small. In such cases the more suitable values of $a_1$ would be the real part of these complex roots and if this is substituted in equation (4.14) equation (4.15) and (4.16) will give $+$ve values of $a_2$ and $a_3$. The real part of complex root is not of course an exact root of equation (4.14) and $f_4$ is derived from the resulting potential according to the following expression,

$$f_4 = D_e [3a_1^4 - 12a_1^2 a_2 + 24a_1 a_3]$$ … (4.17)

The programme was designed by Behere and extended Rydberg potential energy curves were successfully drawn for the ground states of several molecules. The Extended Rydberg potential is used to construct the potential curves of all those molecules under study.
4.4.3 The Zavitsas potential energy function

The Morse potential is \( U_M(r) = D_e [1 - \exp (-\beta_M x)]^2 \)

where \( x = r - r_e \)

This potential function is a modification of Morse function in which the constants \( \beta_M \) is not a constant but varies with \( r \). Moreover the function uses the electronegativity of the constituent atoms forming a diatomic molecule.

The function is expressed as

\[
U_z(r) = D_e \exp (-2\beta_+x) - 2 \exp (-\beta_-x) \quad \ldots \quad (4.18)
\]

Where \( x = r - r_e \), \( D_e \) is dissociation energy. Plus sign indicates \( r > r_e \) and minus sign indicates \( r < r_e \).

\[
\beta_+ = \beta_M(1 + a_1 u^{1/2} + a_2 u^{1/2} + a_3 u^{3n} + a_4 u^{5n}) \quad \ldots \quad (4.19)
\]

and

\[
\beta_- = \beta_M(1 + m u^{1/2}) \quad \ldots \quad (4.20)
\]

\( \beta_M \) is Morse constant,

\[
\beta_M = (2\pi^2 c\mu\omega^2/hD_e)^{1/2} = 0.006513 \omega_e (\mu/D_e)^{1/2} = 8.486 (\kappa_N)^{1/2} \ldots \quad (4.20)
\]

Where \( \kappa_N = \kappa_e/D_e \); \( \kappa_e = 4\pi^2 \mu \omega^2 = 5.8923 \times 10^{-7} \) milli dynes \ldots \quad (4.21)

\[ u = \exp(-2\beta_M x) - 2 \exp (-\beta_M x) + 1 \quad \ldots \quad (4.22) \]

\[ a_1 = -0.32m; a_2 = 0.15; a_3 = 0.2 - 0.6m \; \text{and} \; a_4 = (0.21-3m) / (\Delta \chi)^2 \ldots \quad (4.23) \]

\[ m = -0.025r_e + 0.70\exp (-7.41 \times 10^3 \kappa_N r_N) / z_1 z_2 + 0.042 |\Delta \chi| \ldots \quad (4.24) \]

\[ r_N = (r_e/D_e) \] and \( \Delta \chi = |e_1 - e_2| \) where \( e_1 \) and \( e_2 \) are electronegativities of constituents diatoms on Pauling scale.

\[ n = 0.70 - 0.03r_e + 0.096 / ((10^3 \kappa_N r_N - 0.3) + 0.55 |\Delta \chi|^2 / r_e^{1/2} \ldots \quad (4.25) \]
In all these expressions $D_e$ is kcal/mol. and $r_e$ is in Å.

$Z_1$ and $Z_2$ are the effective nuclear charges. For In and Cl these are 3.45 and 5.75 respectively. [91]

### 4.4.4 Computations

The ground states of other group III A Indium halides and group III A metal chloride molecules are also studied which are of InF, InCl, InBr, InI, BCl, AlCl, and GaCl. The spectroscopic constants of all these molecules are given in Table 4.1. The RKR data of these ground states are used to construct the potential energy curves employing H-H, extended Rydberg and Zavitsas potential functions. In Table 4.2 various parameters required for these computations are given. The data of RKR curves of different electronic states are presented in Tables 4.3(b), 4.8, 4.9. The RKR data i.e. the turning points and corresponding potential energies for different vibrational levels of InF, InCl, InBr, InI, BCl, AlCl, and GaCl and the potential energies calculated using H-H, extended Rydberg and Zavitsas functions along with % deviation from RKR are shown in Tables 4.3(a)-4.3(g) respectively.

Fig. 4.1, 4.14, and 4.15 show RKR curves of $X^1Σ^+$, $A^3Π_0$, and $B^3Π_1$ states respectively. Fig. 4.1 (a), 4.2 (a), 4.3 (a), 4.4(a), 4.5(a), 4.6(a), and 4.7(a) show the comparisons of H-H, extended Rydberg and Zavitsas potential with their corresponding RKR curves for the ground states of InF, InCl, InBr, InI, BCl, AlCl, and GaCl. Below 4.1(a), 4.2(a), 4.3(a), 4.4(a),
4.5(a), 4.6(a) and 4.7(a) curves their corresponding errors curves. 4.1(b), 4.2(b), 4.3(b), 4.4(b), 4.5(b), 4.6(b), 4.7(b) are shown at the same abscissa scale. Error curves means % deviations, which are calculated by formula 
\[
\left( \frac{U_{RKR} - U_{potential}}{D_e} \right) \times 100.
\]

4.5 Discussions:

For the study of potential energy curves two series are chosen viz InF, InCl, InBr and InI where the basic radical remains same. The other series comprise BCl, AlCl, GaCl and InCl molecules where the chloride radical remains same. InCl is common in both cases. The purpose will be clear when we will discuss the Reduced Potential energy Curves (RPC). Majority of the PE curves are drawn which shows PE’s around 40% of the De. Specifically InF (39%), InCl (37%), InBr (46%), InI (44%), BCl (54%), AlCl (35%), GaCl (53%).

The Zavitsas Potential energy curves distinctly deviate from RKR. As per discussion with Zavitsas [91], the potential is mainly suitable for covalent molecules rather than ionic molecules. Moreover the electro negativity values of the atoms forming a diatomic molecule also can cause deviations. Pauling [92] values are used in present study. The ionicity goes on increasing from InI to InF. InF is more ionic compared to other molecules in series. The H-H and Extended Rydberg potential functions almost overlap on each other and fall in between the Zavitsas and RKR.
curves. The error comparison shows that nearly 3 to 4% deviations occur in the potential energies from RKR values.

4.6 The Reduced potential curves

4.6.1 Construction of RPC

A novel method of constructing the potential energy curves was suggested by Jenc [93-102]. This method uses the RKR data to construct the potential energy curves. The name reduced comes because the two parameters in which curves is plotted are not same as of other conventional potential functions in which potential energy \( U \) is in \( \text{cm}^{-1} \) and internuclear separation \( r \) is in \( \text{Å} \) units. On the other hand in the present method, the curve is plotted between two variables \( u \) and \( \rho \) which are as follows,

\[
u = \frac{U}{D_e} \quad \text{and} \quad \rho \]

\[
\rho = \frac{r - [1 - \exp(-r/\rho_{ij})] \rho_{ij}}{r_e - [1 - \exp(-r/\rho_{ij})] \rho_{ij}} \quad \ldots \quad (4.26)
\]

Where \( D_e \) is dissociation energy, \( U \) is a potential energy for any specific \( v \) calculated by the expression.

\[
U = \sum C_i (v + \frac{1}{2})^i \quad \ldots \quad (4.27)
\]

\[
C_1 = \omega_e, \quad C_2 = -\omega_x e, \quad C_3 = \omega_y e \text{ etc.} \quad \ldots \quad (4.28)
\]

The \( r_e \) is equilibrium internuclear separation. The constant \( \rho_{ij} \) can be calculated from the equation.
\[ \rho_{ij} = \frac{r_e - [(3.96) D_e/\kappa_e]^{1/2}}{1 - \exp \left( -r_e / \rho_{ij} \right)} \quad \ldots \quad (4.29) \]

In this equation \( \rho_{ij} \) appears to either side of the equation, so a computer programme was made to solve this equation. \( \kappa_e \) is a force constant. The curve is plotted between \( \rho \) and \( u+1 \).

For \( 0 \leq \rho_{ij} < r_e \). The reduced quantities fulfill the following conditions:

i) \( \rho \geq 0 \) \quad \ldots \quad (4.29 a)

ii) \( \rho = 0 \) for \( r = 0 \) \quad \ldots \quad (4.29 b)

iii) \( \rho = 1 \) for \( r = r_e \) \quad \ldots \quad (4.29 c)

iv) \( \rho \to \infty \) for \( r \to \infty \) \quad \ldots \quad (4.29 d)

v) \( u \leq 0 \) for \( U \leq 0 \) \quad \ldots \quad (4.29 e)

vi) \( u = 0 \) for \( U = 0 \) \quad \ldots \quad (4.29 f)

vii) \( u \to \infty \) for \( U \to \infty \) \quad \ldots \quad (4.29 g)

viii) \( u = -1 \) for \( U = -D_e \) \quad \ldots \quad (4.29 h)

4.6.2 Properties of RPC

1) The RPC’s of different molecules never intersect.

2) The RPC’s of diatomic molecules slightly differing in both atomic numbers coincide.

3) While keeping one atomic number constant a considerable change in the values of other effect, than a relatively small change in the values of both atomic numbers.
4) In general the shape of RPC turns slowly to the right around the minimum while becoming broader.

5) Rare gas molecules do not follow the rule number 2, 3 and 4. The RPC’s of rare gas molecules coincide approximately to each other and form a right hand boundary of the admissible RPC region.

6) All RPC’s including excited state lie in RPC region.

7) The approximate coincidence mentioned in rule 2 and 5 is very accurate in repulsive limb.

It was found that deviations from the above rule in the RPC’s of the diatomic molecules might appear suggesting the possible existence of perturbation in the state or because of erroneous extrapolation of the RKR potential.

4.6.3 Application of RPC

There are several applications of RPC method, which are listed below,

i) Detection of errors in the construction of RKR curve.

ii) Detection of errors in the molecular constants

iii) Detection of errors in the analysis of spectrum.

iv) Detection of errors in the RKR due to perturbations etc.

4.6.4 Inferences drawn from the study of RPC’s

The RPC’s of all these molecules namely InF, InCl, InBr, and InI are drawn. Since their variables are different viz $u+1$ vs $\rho$ they cannot be
compared with RKR or other potential energy function where they are plotted as PE on y-axis and ‘r’ on x-axis. But essentially the nature of RPCs is similar to those of RKR. This will be amply clear from Fig. 4.1 (c),(d) to 4.7(c),(d) that the Reduced potential curves very nearly are similar to those of RKR. In other words RPC remic the RKR curves. All of them have minima at (1,1). The verification of the RPC rules can be easily seen from the combined diagram of the RPC’s. Refer to Fig. 4.8. The ordering nature can be seen the inner most curve is of InI and then Outer most is of InF. So also is in Fig 4.9 $^{115}\text{In}^{35}\text{Cl}$ is inside and $^{115}\text{In}^{37}\text{Cl}$ outside. Infact isotopes have a very small effect on RPC’s. RPC’s of many of the isotopic species actually coincide which will be clear from Fig 4.11, 4.12, and 4.13 wherein the RPC’s of various isotopic species of InCl (either change in Cl isotope or In isotope) are plotted. Fig 4.10 shows the combined RPC of BCl, AlCl, GaCl and InCl. Here the Cl is same and basic radicals are different but from same group in periodic table IIIA. Here also the order is followed. The curve of BCl is inside and that of InCl is outside. RPCs of AlCl and GaCl fall inside as per the atomic weight of Al and Ga.