Chapter-III

POTENTIAL ENERGY FUNCTIONS

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3.1 Account on Potential Energy Curve:

The simple conditions for a function to represent potential energy are:

1. It must show minimum at the equilibrium internuclear distance;
2. It has a sharp rise towards infinity as the nuclei are brought closer together; and
3. It has a less sharp rise towards dissociation limit as the separation is increased.

In practice, it is very difficult to obtain a potential energy function, which will satisfy the above conditions. Hence, some form for potential energy function should be adopted. In this connection, a number of potential energy functions are suggested, making use of energy levels themselves and quantum mechanical methods. These functions have some good points as well as limitations.

Varshini[1] has studied some of these functions and discussed their merits and demerits. His discussion is in terms of the parameters F, G and Δ. The potential energy U(r) of a diatomic molecule can be expressed as:

$$U(r) = \frac{1}{2!} U''(r)(r-r_e)^2 + \frac{1}{3!} U'''(r_e)(r-r_e)^3 + \ldots \qquad \ldots \qquad (3.1)$$

where, r = the internuclear distance,

r_e = Its equilibrium value,

'x' and 'y' are defined as:

$$x = U'''(r_e)/U''(r_e) \qquad \ldots \qquad (3.2)$$

$$y = U''''(r_e)/U'''(r_e) \qquad \ldots \qquad (3.3)$$

Dunham has shown that

$$\alpha_e = \left[\frac{C_3}{C_2} + 1\right] \frac{6B_e^2}{\omega_e} \qquad \ldots \qquad (3.4)$$

and

$$\mu\omega_e x_e = \left[\frac{15}{8}\left(\frac{C_3}{C_2}\right)^2 - \frac{3}{2}\frac{C_4}{C_2}\right]\left[\frac{h}{8\pi^2 C}\right] \qquad \ldots \qquad (3.5)$$

$$\text{where } C_2 = \frac{U''(r_e)}{2!}, \quad C_3 = \frac{U''(r_e)}{3!}, \quad C_4 = \frac{U'''(r_e)}{4!} \qquad \ldots \qquad (3.6)$$

α_e and $\omega_e x_e$ can be expressed in terms of x, y and μ as follows

$$\alpha_e = -\left[\frac{Xr_e}{3} + 1\right]\left[\frac{6B_e^2}{\omega_e}\right] \qquad \ldots \qquad (3.7)$$

$$\omega_e x_e = \left[\frac{5}{3}X^2 - y\right]\frac{W}{\mu_A} \qquad \ldots \qquad (3.8)$$

where, $W = 2.1078 \times 10^{-16}$

In the above equations, the quantities $\left[\frac{Xr_e}{1} + 1\right]$ and $\left[\frac{5}{2}X^2 - y\right]$ are different for different functions. They can be written as:

$$-\left[\frac{Xr_e}{3} + 1\right] = F, \text{ and} \qquad \ldots \qquad (3.9)$$

$$\left[\frac{5}{2}X^2 - y\right] = G \qquad \ldots \qquad (3.10)$$

F and G can be expressed in terms of dimensionless parameter Δ given by:

$$\Delta = \frac{K_e r_e^2}{2D_e} \qquad \ldots \qquad (3.11)$$

The parameter Δ is called "Sutherland's Parameter" in honour of Sutherland.[2,3] Hence,

$$\alpha_e = F.\frac{6B_e^2}{\omega_e} \qquad \ldots \qquad (3.12)$$

$$\omega_e x_e = G.\frac{W}{\mu_A r_e^{2}} \qquad \ldots \qquad (3.13)$$

With the help of equations (3.2), (3.3), (3.7) and (3.8), α_e and $\alpha_e x_e$ can be calculated. These calculated values of α_e and $\omega_e x_e$ can be compared with experimental values. Varshini used different potential energy functions and showed that $\omega_e x_e$ can be calculated to a greater degree of accuracy than α_e. A function which may be useful for $\omega_e x_e$ may fail completely for α_e.

On the basis of 23 diatomic molecules studied by Varshini, the functions in order of increasing accuracy are listed below:

For α_e:
1. Morse,[4] Poschl-Teller,[5] Rosen-Morse,[6] Frost-Musulin,[7,8]
2. Rydberg,[9,10]
3. Varshini III, VI

For $\omega_e x_e$:
1. Morse, Poschl-Teller, Rosen-Morse, Frost-Musulin, Varshini III, VI.

2. Rydberg
3. Lippincott,[11,12] Varshini VII

Thus, for overall representation of the P.E.Curves, the Rydberg, Varshini III and VI functions are most useful. The best values of α_e and $\omega_e x_e$ are obtained from $\alpha_e = (0.11\Delta + 0.36)\ 6B_e^2/\omega_e$, $\omega_e x_e = (5\Delta + g)\ W/r_e^2\mu_A$, using $\Delta = k_e r_e^2/2De$. Above equation can be transferred to $De = 5Wk_e r_e^2/(2\omega_e x_e r_e^2\mu_A - 9W)$ For estimation of dissociation energies, this equation deserves to be employed in preference to $De = \omega_e^2/4\omega_e x_e$.

3.2 Different Forms of Potential Energy Function:

The simplest physical picture of potential energy curve gives minimum at the equilibrium internuclear separation, a sharp rise towards infinity as the nuclei are brought closer and a less sharp rise towards dissociation limit as the separation is increased. In practice, it is very difficult to find a simple mathematical expression representing the potential energy as a function of internuclear separation and hence, it is necessary to adopt some form for compromise.

The potential energy curve can be constructed by two ways:

1. By using experimentally observed energy levels;
2. By quantum mechanical methods.

Oldenberg,[13] Rydberg and Klein[14] have plotted potential energy curve by making use of energy levels and found that the methods are laborious and cannot be applied accurately at low vibrational quantum numbers. Rees,[15,16] formulated the Klein-Rydberg method which enables the evaluation of potential energy curve accurately in the region of minimum. It is somewhat impossible to reach a sufficiently accurate potential energy curve due to the mathematical and computational difficulties. Lippincott and Varshini have formulated criteria for a good potential function. But a single potential function cannot satisfy all these conditions simultaneously. Hence, it is suggested that there is no general potential function applicable to molecules.

3.2.1 The Morse Function:

The Morse Function is the most useful function for plotting approximate potential energy curve. It may be written in several different forms. But the most convenient form is given by:

$$U = De(1-e^{-2\beta\xi})^2 \qquad \ldots \qquad (3.14)$$

where, $\xi = \dfrac{r - r_e}{r_e}$

De = the dissociation energy,

β is a constant given by $\beta = \dfrac{\omega_e}{4(B_e De)^{\frac{1}{2}}}$

ω_e, B_e are vibrational and rotational constants.

The equilibrium internuclear distance is given by: $r_e = \frac{4.1053}{\sqrt{B_e \mu_A}} \times 10^{-8}$ cm, when their expression is substituted in Schrodinger Wave Equation. The resulting wave expression for vibrational energy takes the required form, i.e. $G(v) = \omega_e(v+\frac{1}{2}) - \omega_e x_e (v+\frac{1}{2})^2$ with $\omega_e x_e = \omega_e^2/4De$.

Good Points:

1. The Morse Function leads the potential curve of correct general shape, with its minimum at the equilibrium internuclear distance and going smoothly to the dissociation limit as 'r' increases;

2. Since only three spectroscopically determined paramters, B_e, ω_e and De are required, the function can often be used for molecular states for which spectroscopic data are limited.

Limitations:

1. As equilibrium internuclear distance tends to zero, the potential energy given by Morse Function rises to a very high value, but remains finite. But in practice, this defect is not so important.
2. As the function involves a small number of parameters, the function in its simple form, cannot be adopted to give more accurate fit which may be justified by more

precise data.

It is important to know that in the Morse function, the dissociation energy is measured from minimum of the potential energy curve, not from the lowest real vibrational level. Therefore, the dissociation energy is slightly greater than the true dissociation energy, (D_0) measured from the lowest real vibrational energy.

3.2.2 The Dunham Function:

According to simple harmonic oscillator approximation the potential energy curve in the region of minimum may be considered to be a parabolic form. But to a higher approximation, the curve departs from parabolic form. This departure may be represented by a power series. Representing potential energy as a function ξ, Dunham[17] introduced the function of the form as follows:

$$U = a_0\xi^2(1+a_1\xi + a_2\xi^2 + a_3\xi^3 + \ldots) \quad \ldots(3.15)$$

where, $\xi = \frac{r-r_e}{r_e}$

Dunham used the Wentzel-Brillouin-Kramers Method of solving wave equations to derive energy levels and gave expressions for a_0, a_1, a_2, etc., in terms of rotational and vibrational constants:

$$a_0 = \omega_e^2/4B_e \quad \ldots \quad (3.15\text{-a})$$

$$a_1 = -1-\omega_e\alpha_1/6B_e^2 \quad \ldots \quad (3.15\text{-b})$$

$$a_2 = 5a_1^2/4 - 2x_e\omega_e/3B_e \quad \ldots \quad (3.16\text{-c})$$

$$a_3 = \alpha_2.\omega_e^2/30B_e^3-1-2a_1 + \frac{3}{5}a_2 + \frac{13}{5}a_1a_2 - \frac{3}{2}a_1^2 + \frac{3}{2}a_1^3 \quad \ldots \quad (3.15\text{-d})$$

Further, terms may be evaluated. But they are more complex. These expressions are only approximate, owing to the use of the Wentzel-Brillouin-Kramers Method of solving the wave equations. Dunham investigated errors resulting from their approximation. For H_2 small correction terms are required. for hydrides, the error is almost negligible.

Good Points:

1. The function can be used to give very accurate results in the region of minimum.
2. The function is capable of giving more accurate results than that of Morse function in the region of minimum.
3. The function can be used to give lower part of the curve when the dissociation energy is not known.

Limitations:

1. As the series is not convergent, the function is not suitable for large values of internuclear distance.
2. As the internuclear distance becomes infinite, the potential energy obtained from this function tends to plus or minus infinity instead of going to dissociation limit.

3.2.3 The Hulbert-Hirschfelder Function:[18]

A number of potential energy expressions were suggested. These mostly endeavour to obtain the advantage of the Morse Function, combined with greater flexibility and accuracy and introduce additional parameters. Manning and Rosen[19], Poschl and Teller, Hylleras, [20,21,22] and Coolidge, James and Vernon[23] have introduced useful potential energy functions. Hulbert and Hirschfelder[18] have reviewed and compared these potential energy functions. Then by using these results, they modify Morse potential energy function and put forward one of their own potential energy function given by:

$$U = De[(1-e^{-x})^2 + x^3e^{-2x}(1-bx)] \qquad \ldots \qquad (3.16)$$

where,

$$x = 2\beta\xi = \frac{\omega_e}{2(B_eD_e)^{\frac{1}{2}}} \cdot \frac{r-r_e}{r_e}$$

$$c = 1 + a_1(De/a_0)^{\frac{1}{2}}$$

$$b = 2 + (\frac{7}{12} - D_ea_2/a_0)/C$$

The constant β is the same as that of Morse function and the constants a_0, a_1 and a_2 have the same values as in Dunham's function. The spectroscopically determined constants used are B_e, ω_e, $x_e\omega_e$, α_1 and De.

Good Points:

1. The function involves just those five parameters which are most readily obtained from the study of band spectrum.

2. This is probably the best expression for plotting the potential energy curve when the above constants are known.

Limitations:

1. As it is in modified Morse function, it has the limitations of Morse function.
2. It requires the knowledge of dissociation energy.
3. It is only suitable for potential curves of fairly conventional shape.

With only a few exceptions, this potential curve lies above the Morse curve. The work of Tawde and Gopalkrishnan[24] on the transition probabilities in the C_2 (swan) system suggests that this function is only satisfactory in the region $r > r_e$.

3.2.4 Mecke-Sutherland Function:

Mecke[25] and Sutherland[23] suggested the function of the form:

$$U = \frac{a}{r^m} - \frac{b}{r^n} \qquad \dots \quad (3.17)$$

Here, both the attrative and repulsive terms are of reciprocal type. This type of function was used before by Gruneisen,[26] Mie[27] etc. for forces in the solid state. A special case (m = 2, n=1) has been treated by Fues.[28] Such a type of function was used by Baughan[29] for the interaction between non-bonded atoms.

From this function,

$$De = \frac{(a)}{r_e^m} \quad \frac{(m-n)}{n} = \frac{b}{r_e^n} \quad \frac{(m-n)}{m}$$

$$ke = am(m-n)/r_e^{m+2} = bn(m-n)/r_e^{n+2}$$

$$2\Delta = k\ r\ ^2/De = mn$$

$$\alpha_e = (m+n)\ .\ \frac{2B_e{}^2}{\omega_e}$$

$$\omega_e x_e = \left[\frac{2}{3}m^2 + \frac{7}{3}mn + \frac{2}{3}n^2 + 4(m+n) + 4\right]\frac{W}{r_e^2\mu_A}$$

This function is a four constant function and their values are determined from k_e, r_e, De and α_e.

Sutherland later on modified this function. He replaced r by (r–d), i.e. $U = \frac{a}{(r-d)^m} - \frac{b}{(r-d)^n}$

This modified function can be used to derive a series of fruitful relations connecting various molecular parameters by making certain assumptions regarding a, d, m and n.

3.2.5 Linnet Function:

Linnet[30,31] suggested a function of the form:

$$U = \frac{a}{r^m}\ be^{-nr} \qquad \ldots \qquad (3.19)$$

From this function he derived following relations:

$$De = \frac{a}{r_e^m}\left[\frac{m-nr_e}{nr_e}\right]$$

$$k_e = am\ (m + 1 - nr_e)/r_e^{m+2}$$

$$\therefore\ k_e r_e^{m+2} = ma + \frac{m^2 D_e r_e^m}{1+D_e r_e^m/a}$$

$$\omega_e x_e = \left[\frac{5}{3}\left\{\frac{20-(nr_e^2)}{4-nr_e}\right\}^2 - \left\{\frac{120-(nr_e)^3}{4-nr_e}\right\}\right]\frac{2,098}{r_e^2\mu_A}$$

Linnet traced the regularities in the value of a and extended the function to other periods. The funtion gives rise to a low maximum between $r=r_e$ and $r=\infty$, this behaviour is found with $^1\Sigma_g^+$ and $^3\Pi_g$ states of N_2. But there is no experimental evidence for such a maximum in these states.

3.2.6 Lippincott Function:

Lippincott has suggested the following function and has given a semitheoretical justification for it,

$$U = D_e[1-\exp(-nP^2/2r)]\ [1+af(r)] \qquad \ldots \qquad (3.20)$$

Here, f(r) is the function of internuclear distance such that for r=0, f(r)=∞ and for r=∞, f(r)=0.

Lippincott considered the term f(r) to be unimportant and neglected it.

$$\therefore\ U = D_e[1-\exp(-nP^2/2r)] \qquad \ldots \qquad (3.21)$$

This function gives, $n = k_e r_e/D_e$

$$_e = 0$$

$$_e x_e = (3nr_e + 3)\frac{W}{r_e^2\mu_A}$$

As this function (3.21) gives α_e to be zero, Lippincott used function (3.20) with:

$$af(r) = -a(r_e/r)^6[1-\exp(-b^2nr''/2r_e'^2)]^{\frac{1}{2}} + a(r_e/r)^{12} \quad X$$

$$[1-\exp(-b^2nr''/2r_e'^2)]$$

and derived the following equation:

$$D_e = \omega_e^2/2nr_eB_e$$

$$\alpha$$

$$\alpha_e = ab\left(\frac{nr_e}{2}\right)^{\frac{1}{2}} \cdot \frac{6B_e^2}{\omega_e}$$

$$\omega_e x_e = 1.5B\ (0.25+nr/4+ab(nr_e/2)^{\frac{1}{2}} + (5a^2b^2-ab^2)nr_e/2]$$

It is observed that the calculated values of α_e and $\omega_e x_e$ are in well agreement with the experimental value.

3.2.7 MRK Potential Function:

Behere[32] attempted the hybrid potential function from Morse, Rydberg and Kratzer.[33] A potential which is linear combination of Morse and Rydberg is suggested by Iyer and Sharma[34], which is re-investigated by Birajdar et al.[35] A potential function which is a combination of Morse and Kratzer was also suggested by Raghuwanshi and Sharma.[36] The Rydberg Kratzer hybrid potential was suggested by Varma and Jha.[37]

The potential which is a combination of Morse, Rydberg and Kratzer is of the form,

$$U = De\{[1-e^{-ap}]^2 - [1+b\rho]e^{-bp} + \frac{\rho^2}{r^2} + 1\} \qquad \ldots \quad (3.22)$$

where, De = the dissociation energy

ρ = $(r-r_e)$

a = Morse parameter given by $a^2 = k_e/2D_e$

b = Rydberg parameter given by $b^2 = k_e/D_e$

k_e = the force constant.

Equation (1) can be considered either in Morse form or in Rydberg form:

$$U(r) = De\{[1-e^{-ap}]^2 - [1+\sqrt{2}ap]e^{-\sqrt{2}ap} + \frac{\rho^2}{r^2} + 1\} \quad \text{Morse Form} \quad \ldots \quad (3.23)$$

$$U(r) = De\{[1-e^{-bP/\sqrt{2}}]^2 - [1+b\rho]e^{-bp} + \frac{\rho^2}{r^2} + 1\} \quad \text{Rydberg Form} \quad \ldots \quad (3.24)$$

The potential function (3.22) satisfies the criteria in order to be a suitable potential function. As suggested by Varshini, α_e and $\omega_e x_e$ can be calculated for a given potential as follows:

$$\alpha_e = [\frac{xr_e}{3} + 1] \qquad \text{where, } x = \frac{U'''(r_e)}{U''(r_e)} \qquad \ldots \quad (3.25)$$

$$\omega_e x_e = [\frac{5}{3}x^2 y]\frac{W}{\mu_A} \qquad \text{where, } y = \frac{U^{IV}(r_e)}{U''(r_e)} \qquad (3.26)$$

The values of U", U"', U^{IV} at $r = r_e$ for Morse form and Rydberg form are obtained. Using Morse function (3.23), the expressions for 'x' and 'y' are given as follows:

$$x = \frac{a^3 r_e^3 (3+2\sqrt{2}) + 6}{(2a^2 r_e^2 + 1) r_e}, \quad y = \frac{13 a^4 r_e^4 + 36}{(2a^2 r_e^2 + 1) r_e}$$

The relations between Sutherland parameter Δ, the Morse parameter a and Rydberg parameter b are given by:

$$\Delta = 2a^2 r_e^2 - 1 \text{ and } \Delta = b^2 r_e^2 + 1$$

so that

$$a r_e = \left(\frac{\Delta-1}{2}\right)^{\frac{1}{2}}, \quad a^2 r_e^2 = \left(\frac{\Delta-1}{2}\right) \text{ and } a^3 r_e^3 = \left(\frac{\Delta-1}{2}\right)^{3/2}, \text{ etc.}$$

$$b r_e = (\Delta-1)^{\frac{1}{2}}, \quad b^2 r_e^2 = (\Delta-1), \quad b^3 r_e^3 = (\Delta-1)^{3/2}, \text{ etc.}$$

Using relation (4),

$$\alpha_e = \left[\frac{a^3 r_e^3 (3 + 2\sqrt{2}) + 6}{3(2a^2 r_e^2 + 1)} - 1\right] \frac{6B_e^2}{\omega_e}$$

In terms of Δ,

$$\alpha_e = \left\{0.6869 \frac{(\Delta-1)^{3/2}}{\Delta} + \frac{2}{\Delta} - 1\right\} \frac{6B_e^2}{\omega_e} \qquad \ldots \quad (3.27)$$

Using relation (3.26)

$$\omega_e x_e = \left\{\frac{5}{3}\left[\frac{a^2 r_e^3 (3+2\sqrt{2}) + 6}{(2a^2 r_e^2 + 1)}\right]^2 - \left[\frac{13 a^4 r_e^4 + 36}{2a^2 r_e^2 + 1}\right]\right\} \frac{W}{\mu_A r_e^2}$$

substituting the values of $a r_e$, $a^2 r_e^2$, $a^3 r_e^3$, etc., in terms of Δ and after simplification, we get,

$$\omega_e x_e = \left[3.8272 - 14.7316 - \frac{18.0184}{\Delta} + \frac{52.9228}{\Delta^2} + \frac{42.1232(\Delta-1)^{3/2}}{\Delta^2}\right] \frac{W}{\mu_A r_e^2} \quad (3.28)$$

relations (6) and (7) gives the values of α_e and $\omega_e x_e$ using potential in Morse form.

The relations (3.27) and (3.28) are applied to a number of diatomic molecules. The results are listed in Tables (3.9a) and (3.9b). The experimental values of α_e and $\omega_e x_e$ and other molecular constants required to calculate α_e and $\omega_e x_e$ are taken from Herzberg.[38]

From Table (3.9a), it can be seen that the values of α_e and $\omega_e x_e$ are lowered down by MRK functions. Table (3.9b) gives the comparison of percentage errors of few potentials and MRK potential. It is observed that MRK gives considerable average % error in α_e and $\omega_e x_e$ compared to other potentials.

3.3 RKRV Procedure for Obtaining Classical Turning Points:

The previous methods of plotting potential energy curves (3.2.1 to 3.2.6) uses a mathematical expression involving derived molecular constants. Here, it is assumed that the vibrational levels can be represented as a single rapidly convergent series in (V+½), as

$$G(v) = \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 + x_e\omega_e(v+\tfrac{1}{2})^3 + \ldots \qquad \ldots (3.29)$$

But this is not always possible. For a number of excited states, there are definite signs for abrupt change in the rate of convergence of vibrational levels. Such levels are represented by two power series in (v+½), one below certain value of 'v' and the other above this value of 'v'. Hence, the knowledge of energy levels themselves rather than some derived formula is essential, i.e. potential energy curve should be plotted by making use of energy levels. Rydberg gave a graphical procedure of doing this and the method was further developed by Klein. Klein's method has been used with success by Rosenbaum[39] and by Almy and Beiler[40] for the upper electronic states of LiH and KH.

This method is suitable for higher vibrational levels and not for lower vibrational levels. Klein has derived the following function:

$$S(U,K) = \frac{1}{\Pi\sqrt{2\mu}} \int_0^{I'} [U-E(I,k)]\, dI \qquad \ldots \qquad (3.30)$$

Here, U = the potential energy.

E(I,k) = Energy of vibration and rotation expressed as a function of action variable I,

k = square of angular momentum/2μ

I' = the value of I for U = E

Klein showed that, $I = (u+\frac{1}{2}).h$

$k = [k(k+1)h^2]/8\Pi^2\mu$

Rees provided analytical expressions for f and g of Klein.

If $f = \frac{ds}{du}$ and

$g = -\frac{ds}{dk}$

then, the maximum and minimum values of internuclear distance for vibrating moleculre are given by:

$$r_{max} = (f/g + f^2)^{\frac{1}{2}} + f$$
$$r_{min} = (f/g + f^2)^{\frac{1}{2}} - f \qquad \ldots \quad (3.31)$$

These are the classical turning points. For a normal potential curve (the rotationless state), the values $f = \left[\frac{ds}{du}\right]_{k=0}$ and $g = -\left[\frac{ds}{dk}\right]_{k=0}$ are required. These values are obtained as follows:

1) <u>To obtain f</u>:

a. The vibrational energy levels, obtained from the measurements of band origin are tabulated and a level with vibrational quantum no, v=i and energy U_i is selected.

b. From U_i, the energy of all levels with U<i is subtracted and a series of values of the quantity $(U_i - E_v)$ is obtained.

c. Then $(U_i - E_v)^{\frac{1}{2}}$ are plotted against $(v+\frac{1}{2})$ and from this graph, the area under the curve between v=0 to v=i+½ is obtained.

d. This area multiplied by the factor $h(hc)^{\frac{1}{2}}/[\Pi(2\mu)^{\frac{1}{2}} \simeq 1.631 \times 10^{-23}/\mu_p$ gives the value of S for U_i.

e. Similarly, values of S are obtained for different values of U_i. S is plotted against U to get ds/du.

2) <u>To obtain g</u>:

Here, the same procedure is repeated. Only $(U_i - E_v)$

is replaced by $[U_i - (E_V + E_r) = [U_i - (E_V + B_V K(K+1)]$. A series of S and U for different values of K is obtained. S is plotted against K at any selected U. 'g' is obtained from the slope of this graph at k=0. But we know that $E_r << E_V$ and and hence, no accurate results are obtained even if a very large scale graph is used. Therefore, replacing ds/dk by $\Delta s/\Delta k$, more accurate results are obtained as follows:

1) $(U_i - E_v)^{½} - [U_i - (E_v + B_v k(k+1)]^{½}$ is plotted against $(v+½)$
2) The area beneath the curve multiplied by the factor $h(hc)^{½}/[\Pi(2\mu)^{½}$ gives $- \Delta S$
3) $\Delta K = K(KH)h^2/8\Pi^2\mu \approx 3.350 \times 10^{-31} K(K+1)/ \mu_A$
4) Hence, $g = -\Delta S/\Delta K$ can be evaluated.

Good Points of Klein's Method:

1. Here, the resulting curve depends upon experimentally determined energy levels.
2. It does not depend upon the derived constants or any assumption about them.

Limitations:

1. The method is based upon classical mechanics and it is unsuitable for lower vibrational levels. For low vibrational levels, i.e. below about $v=5$, the graphical method has insufficient accuracy as there are no enough points.

2. 'F' cannot be determined with great accuracy. The percentage errors in r_{max} and r_{min} are less as compared with the errors in f and g. But the effect is considered to be unimportant, if the results reliable to 5% are required.

3.4 True Potential Energy Curve:

3.4.1 Extended Rydberg Potential Energy Curve.

The extended Rydberg potential as suggested[41] which is of the form:

$$U = De[1 + a_1\rho + a_2\rho + a_3\rho]e^{-a_1\rho} \qquad \ldots \quad (3.32)$$

where, De = the dissociation energy (not D_0°)

$\rho = r - r_e$

a_1, a_2, a_3 = are some constants which can be evaluated if we can evaluate the constants f_2, f_3 and f_4 given as follows:

$$f_2 = 4\Pi^2 m\omega_e{}^2 c^2$$

$$f_3 = \frac{-3f_2}{r_e}\left(1 + \frac{\alpha_e\omega_e}{6B_e^2}\right) \qquad \ldots \quad (3.33)$$

$$f_4 = \frac{f_2}{r_e^2}\left[[15\left(1 + \frac{\alpha_e\omega_e}{6B_e^2}\right)^2 - \frac{8\omega_e x_e}{B_e}\right]$$

where m = the reduced mass

c = the velocity of light.

and all other constants have the usual meaning.

Here, f_2 comes out in a unit of a Joules $A^{\circ -2}$. As in the expression for f_3 and f_4, r and r_e^2 are in denominator, f_3 comes out in a unit a Joules $A^{\circ -3}$ and f comes out in a unit of a Joules $A^{\circ -4}$. $\alpha_e \omega_e / B_e^2$ and $\omega_e x_e / B_e$ are dimensionless quantities.

When the constants f_2, f_3 and f_4 are obtained, then we have to solve the following quartic equation for a_1, i.e. $De a_1^4 - 6f_2 a_1^2 - 4f_3 a_1 - f_4 = 0$.

In this equation, De is to be taken in eV. This quatric equation has four roots. The largest positive root should be taken as a_1 and then a_2 and a_3 are evaluated as follows:

$$a_2 = \tfrac{1}{2}(a_1^2 - f_2/D_e)$$
$$a_3 = a_1 a_2 - 1/3 a_1^3 - \frac{f}{6D_e} \qquad \ldots \quad (3.34)$$

Once all the constants a_1, a_2 and a_3 are obtained, we come back to the equation for U. Various values of r, i.e. turning points obtained through RKR calculations are substituted in the expression for U along with a_1, a_2 and a_3 and U values are calculated. These U values are then compared with G(v).

We have applied their method to X state of HoF and $X^2\Sigma$ state of YbF and the results are reported in Tables (3.10) and (3.11).

3.4.2 Rapid Method to Construct True Potential Energy Curve:

It is very laborious to obtain classical turning points from RKR and RKRV methods. To avoid this, Vaidyan and Santaram[42] have suggested a rapid method to construct potential energy curve based on RKR potential which involves empirical relations. Connecting 'r' and 'U', Vaidyan et al.[43,44] recasted the Morse function in order to obtain an equation of a straight line for the empirical relations in the form

$$\log\,[\{\omega_e \pm (4\omega_e x\ U)^{\frac{1}{2}}\}/\omega_e] = -\alpha' r + \alpha r_e \qquad \ldots \qquad (3.35)$$

where, $\alpha' = 2.3036$, α and r_e are constants.

The equation of straight line can be obtained by replacing $-\alpha'$ by m and $(\alpha r_e + \log\omega_e)$ by C. The resulting equation is of the form:

$$\log[\omega_e \pm (4\omega_e x_e U)^{\frac{1}{2}}] = mr + c \qquad \ldots \qquad (3.36)$$

For r_{max} and r_{min}, we can write,

$$\log[\omega_e + (4\omega_e x_e U)^{\frac{1}{2}}] = m_+ r + c_+ \qquad \text{For } r < r_e \quad - (3.37)$$

and

$$\log[\omega_e - (4\omega_e x_e U)^{\frac{1}{2}}] = m_- r + c_- \qquad \text{For } r < r_e \quad - (3.38)$$

These equations result in the negative value of m. From Morse function, we note that α should be positive, which indicates that m being negative is appropriate. Geometrically, m represents the slope of the straight line. In the RKRV procedure for the determination of classical turning points, the half width of the potential curve is given by:

$$f = \frac{r_{max} - r_{min}}{2}$$

where, $(r_{max}-r_{min})$ is given by:

$$(r_{max} - r_{min}) = \left[\frac{h}{8\Pi^2 \mu C \omega_e x_e}\right]^{\frac{1}{2}}$$

$$\{\ln\{\omega_e + (4\omega_e x_e U)^{\frac{1}{2}} - \ln\{\omega_e - (4\omega_e x_e U)^{\frac{1}{2}}\}\}$$

These expressions are similar to the expressions (3.37) and (3.38), 'r' values corresponding to any energy values. U can be obtained if m and c are known. The constants m and c are obtained by using 'r' values evaluated using RKRV procedure corresponding to two energy states. After knowing m and c values, the evaluation of 'r' values is simple and rapid.

From the expressions (3.37) and (3.38), it is observed that the applicability of Morse function to a particular electronic state requires that:

1) $m_+ = m_-$

2) $c_+ = c_-$

The applicability of Morse function to a particular electronic state is tested by plotting the graph of log $[\omega_e \pm (4\omega_e x_e U)^{\frac{1}{2}}]$ versus r. If the graph turns to be a straight line, then the above conditions are satisfied and Morse function is applicable to that particular electronic state. If $m_+ \neq m_-$ the graph deviates from the straight line and represents the

the deviation of Morse Curve from that curve.

RKRV data is used to adjust the Morse function in order to represent an electronic state sufficiently upto that vibrational level at which its energy can be expressed as a quadratic in $(v+\frac{1}{2})$.

In this method, the turning points r_{max}, r_{min} and the equilibrium internuclear distance of the electronic state, which obey Morse function, can be related by the equation:

$$e^{\alpha r_e} = \frac{2}{e^{-\alpha r_{max}} + e^{-\alpha r_{min}}}$$

With the help of the above equation, the shifted r'_e corresponding to Morse Constant α', which is mean of α_1 and α_2 can be determined making use of RKRV turning points.

Recently, Reddy and Reddy[45] modified the method due to Vaidyan and Santaram. In the latter method, one needs two r_{min} and two r_{max} values from RKRV method, to evaluate the constants m and c. Reddy and Reddy gave a procedure in which r values from RKRV are not needed to evaluate the true turning points. They have obtained the following relations:

$$m_{\pm} = \ln\left[\frac{\omega_e + (4\omega_e x_e U_4)^{\frac{1}{2}}}{\omega_e + (4\omega_e x_e U_3)^{\frac{1}{2}}}\right] / \ (r_4 - r_3)$$

where,

$$r_4 - r_3 = \left\{\left[\frac{b_1}{2\sqrt{g_1}} - \frac{b_2}{2\sqrt{g_2}}\right] K + (\sqrt{g_1}-\sqrt{g_2}) \pm (x_4-x_3)\right\} r_e$$

in which

$$b_1 = \frac{3.75}{h_1} - \frac{b'}{h_1^2} + 135P^2$$

$$g_1 = 18P^2 + \frac{1}{h_1}; \quad h_1 = 1-3m \text{ and } b' = 3.75-12.15m$$

$$b_2 = \frac{2.917}{h_2} - \frac{b''}{h_2^2} + 82P^2$$

$$g_2 = 14P^2 + 1/h_3; \quad h_2 = 1 - 7m/3 \text{ and } b'' = 2.917-7.35m$$

$$x_4-x_3 = P[0.501 + 5K + 43.1K^2]$$

$$P = (B_e/\omega_e)^{1/2}, \quad m = \alpha_e/B_e \text{ and } K = \omega_e x_e/\omega_e$$

$$\text{For } r>r_e, \ \ln[\omega_e - (4\omega_e x_e U_3)^{1/2}] = m_+ r_3 + c_+$$

$$r<r_e, \ \ln[\omega_e - (4\omega_e x_e U_3)^{1/2}] = m_- r_4 + c_-$$

$$\text{for } r\pm, \ r_3 = [(b_2 k/2\sqrt{g_2}) + \sqrt{g_2} \pm P(3.74166+10.9132K+49.273K^2)]$$

Knowing the values $m_\pm$ from equations (3.40) and (3.41), one can evaluate the true turning points rapidly by varying 'U' value in the Vaidyan and Santaram method.

We have applied the rapid method to construct the true potential energy curve for the electronic states of x and B of xef, $A^2\Delta_{5/2}$, $B^2\Delta_{5/2}$ and $X^2\Delta_{5/2}$ states of PtH and PtD, X and A states of HoF, $X^2\Sigma$ and $A^2\Pi_{3/2}$ states of YbF, X state of LuF and SiTe, $A^3\Pi_o^+$, $B^2\Pi^+$ and $X'\Sigma^+$ states of InBr.

The constants 'm' and 'c' in equation (3.37) and (3.38) which depend upon molecular geometry can be determined by two methods:

1) A graph of $\log[\omega_e \pm (4\omega_e x_e U)^{\frac{1}{2}}]$ versus r is plotted. The slope corresponds to 'm' and the intercept corresponds to 'c' values.
2) Using equations (3.37) and (3.38), the constants are determined using least-square method. For this, we have to use vibrational energy U in different vibrational states, the accurate RKRV data of vibrational energies, spectroscopic constants available in literature.

We have computed the values of 'm' and 'c' for the above mentioned states. The graphs of $\log[\omega_e \pm (4\omega_e x_e U)^{\frac{1}{2}}]$ versus r are plotted for the above mentioned states and are represented in Figs.(3.1) to (3.7).

The classical turning points are evaluated, for all the states using rapid method and are given in Tables (3.1) to (3.8), along with RKRV values. The constants 'm' and 'c' are given for the corresponding states in each Table. From the table, we can see that the absolute difference $(m_+ - m_-)$ are sufficiently large and hence, the graphs deviate from straight line. Hence, a new functional relation for these states is used.

3.4.3 Lakshman & Rao Method:

Lakshman & Rao[46] constructed a potential energy curve with the help of modified Ree's method. They constructed rotationless potential energy curve. For this, they derived the equations by replacing 'ω_e', '$\omega_e x_e$', 'U', 'B_e' and 'α_e' of Ree's equation by 'ωm', 'ωmXm', 'Um', 'Bm' and 'αm', respectively.

$$f(\mathrm{cm}) = (c^*/\mu\omega mXm)^{\frac{1}{2}} \ln[(\omega^2 m-4\omega mXmU)^{\frac{1}{2}}/\omega m-(4\omega mXmU)^{\frac{1}{2}} \quad \ldots (3.45)$$

$$g(\mathrm{cm}^{-1}) = (\mu/4c^*)^{\frac{1}{2}}(\omega mXm)^{-3/2} \quad X$$
$$\{\alpha m(\omega mXmUm)^{\frac{1}{2}} + (2\omega mXmBm - \alpha m\omega m)$$
$$\ln[(\omega_m^2 - 4\omega mXmUm)^{\frac{1}{2}} / \omega m-(4\omega mXmUm)^{\frac{1}{2}}]\} \quad \ldots (3.46)$$

where, $c^* = 16.8575$

ωm, ωmXm are evaluated using least-square procedure. For this, four vibrational levels are used at a time. The values so obtained are used for middle two levels. The next set of four vibrational levels is used to determine constants for other successive levels.

The method is applied to construct the true potential energy curve for X and B states of XeF, $A^2\Delta_{5/2}$, $B^2\Delta_{5/2}$ $X^2\Delta_{5/2}$ states of PtH and PtD. The values are taken from literature and are reported in Tables (3.1, 3.6 and 3.7) alongwith the values obtained by RKRV method, Rapid method and using functional relations. It is observed that the values are in excellent agreement with the RKRV method.

3.4.4 Functional Relation for Diatomics:

We know that if a graph of $\log[\omega e \pm (4\omega exeU)^{\frac{1}{2}}]$ versus r is a straight line, then Morse function is applicable to that particular electronic state. If a graph deviates from straight line, then Morse function is not applicable for that particular electronic state.

For such electronic states, the following functional formulae are suggested to represent empirical relations connecting r and U.[47]

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

and $$f(U) = Ar^{3/2} + Br + C$$

The constants involved in the functional relation may be determined with the knowledge of RKRV turning points. After knowing these constants, the algebraic expressions are solved for the determination of r values, corresponding to given U Like Vaidyan et al. this method is not simple and rapid. But the method is definitely more accurate than their method.

We have evaluated the constants γ, ρ and C for the entire curve and the final expressions are reported below:

I) Xef:

1) $X_{1/2}$State, $f(U) = -0.4364225476r^2 - 2.438427358r - 0.7728402242$

2) $B_{1/2}$ State, $f(U) = -0.4153787627r^2 - 2.849482089r - 2.12209657$

II) PtH

1) $A^2\,\Delta_{5/2}$ State, $f(u) = -0.4223189803r^2 - 2.065950475r + 1.016500486$

2) $B^2\,\Delta_{5/2}$ State, $f(U) = -0.3905277027r^2 - 1.896836923r + 1.239829934$

3) $X^2\,\Delta_{5/2}$ State, $f(U) = -0.800954252r^2 - 3.367242994r + 0.037148666$

III) PtD

1) $A^2\,\Delta_{5/2}$ State, $f(U) = -0.5000934877r^2 - 2.313645315r + 0.699422677$

2) $B^2\,\Delta_{5/2}$ State, $f(U) = -0.4748879145r^2 - 2.170690995r + 0.8916136613$

3) $X^2\,\Delta_{5/2}$ State, $f(U) = -0.8403833521r^2 - 3.418348434r + 0.068849731$

IV) HoF

1) X State $f(U) = -0.0057172108r^2 - 0.0299752595r + 2.75190141$

2) A State $f(U) = -0.0049610683r^2 - 0.0267819337r + 2.755212934$

V) Ybf

1) $X^2\Sigma$ State $f(U) = -0.0048676451r^2 - 0.0270737176r + 2.665795925$

2) $A^2\Pi_{3/2}$ State $f(U) = -0.0047004015r^2 - 0.0261417908r + 2.667225269$

VI) SiTe

1) X State $f(U) = -0.6315197088r^2 - 3.48238583r - 1.974764376$

VII) LuF

1) X State $f(U) = -0.9128694237r^2 - 4.251925055r - 2.015485929$

VIII) InBr

1) $A^3\Pi_o$ State $f(U) = -1.803071025r^2 - 10.12193385r - 11.64985467$

2) $B^2\Pi$ State $f(U) = -1.603001064r^2 - 9.138871765r - 10.48534958$

3) $X'\,\Sigma^+$ State $f(U) = -0.7376750812r^2 - 4.432917618r - 4.163843781$

Using these expressions, we have computed classical turning points for different electronic states of molecules XeF, PtH, PtD, HoF, YbF, SiTe, LuF and InBr. These results are reported in Tables (3.1) to (3.8).

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‡ ‡ ‡

TABLE 3.1a

Classical Turning Points of X state of XeF

V	U(e) cm^{-1}	RKRV Method		Lakshman & Rao's Method		Rapid Method		Using Functional Relation		Constants and References
		r_{min} (A°)	r_{max} (A°)	r_{min} (A°)	r_{max} (A°)	r_{min} (A°)	r_{max} (A°)	r_{min} (A°)	r_{max} (A°)	
0	110.85	2.237	2.430	2.237	2.430	2.239	2.409	2.237	2.433	Ref: T.V.Ramkrishna Rao and Ramkrishna Reddy.[48]
1	315.60	2.185	2.535	2.185	2.535	2.184	2.572	2.185	2.520	m+ = 0.1478572791
2	497.72	2.152	2.627	2.151	2.626	2.147	2.670	2.140	2.590	c+ = 2.220372821
3	657.21	2.123	2.718	2.121	2.716	2.118	2.739	2.113	2.659	m- = 0.5524149227
4	794.08	2.093	2.813	2.092	2.811	2.096	2.791	2.093	2.774	c- = 1.261029155

TABLE 3.1b

Classical Turning Points of B state of XeF

V	U(e) cm^{-1}	RKRV Method		Lakshman&Rao's Method		Rapid Method		Using Functional Relation		Constants and References
		r_{min}(A°)	r_{max}(A°)	r_{min}(A°)	r_{max}(A°)	r_{min}(A°)	r_{max}(A°)	r_{min}(A°)	r_{max}(A°)	
0	154.15	2.558	2.721	2.559	2.722	2.762	2.673	2.617	2.769	Ref: T.V.Ramkrishna Rao and Ramkrishna Reddy.[48]
1	763.12	2.468	2.834	2.468	2.834	2.698	2.845	2.521	2.863	
2	1360.08	2.414	2.910	2.414	2.910	2.654	2.942	2.460	2.924	
3	1945.35	2.373	2.974	2.372	2.973	2.616	3.013	2.410	2.974	m+ = 0.280675544
4	2519.28	2.336	3.031	2.336	3.031	2.581	3.0701	2.366	3.0189	c+ = 1.832785928
5	3082.21	2.305	3.085	2.305	3.086	2.547	3.119	2.325	3.0609	m− = 1.076628606
6	3634.46	2.278	3.137	2.277	3.136	2.514	3.161	2.288	3.1018	c− = −0.48383398
7	4176.38	2.252	3.187	2.251	3.186	2.482	3.199	2.252	3.1431	
8	4708.29	2.229	3.237	2.227	3.325	2.450	3.232	2.217	3.1860	
9	5230.54	2.204	3.284	2.203	3.283	2.417	3.263	2.183	3.233	
10	5743.46	2.183	3.333	2.181	3.331	2.385	3.291	2.150	3.290	
11	6247.39	2.163	3.382	2.160	3.379	2.351	3.317	2.116	3.382	

TABLE 3.2a

Classical Turning Points of $X^2\Sigma$ State of YbF

V	U(r) cm^{-1}	RKRV Method r_{min} (A°)	RKRV Method r_{max} (A°)	Rapid Method r_{min} (A°)	Rapid Method r_{max} (A°)	Using Functional Relation r_{min} (A°)	Using Functional Relation r_{max} (A°)	Constants and References
0	0.03133	1.95657	2.08154	1.95370	2.07355	1.9612	2.0998	Ref: N.B.Ishwar and B.L.Jha.[49]
1	0.09355	1.91658	2.13381	1.91780	2.1357	1.9207	2.1351	
2	0.15524	1.89064	2.17211	1.89323	2.1783	1.8940	2.1721	
3	0.21637	1.87047	2.20474	1.87339	2.2126	1.8483	2.2037	
4	0.27696	1.85366	2.23412	1.85633	2.2420	1.8554	2.2323	m+ = 0.0053166650
5	0.33700	1.83900	2.26132	1.84119	2.2682	1.8399	2.2590	c+ = 2.690056078
6	0.39650	1.82624	2.28697	1.82747	2.2918	1.82624	2.2843	m− = 0.0092372095
7	0.45545	1.81464	2.31144	1.81485	2.3136	1.81378	2.3088	c− = 2.682123999
8	0.51385	1.80406	2.33499	1.80312	2.3338	1.80150	2.3328	
9	0.57170	1.79430	2.35781	1.79215	2.3527	1.7918	2.3565	
10	0.62901	1.78450	2.38002	1.78181	2.3705	1.78190	2.38002	

TABLE 3.2b

Classical Turning Points of $A^2\Pi_{3/2}$ State of YbF

V	U(r) cm -1	RKRV Method r_{min} (A°)	RKRV Method r_{max} (A°)	Rapid Method r_{min} (A°)	Rapid Method r_{max} (A°)	Using Functional Relation r_{min} (A°)	Using Functional Relation r_{max} (A°)	Constants and References
0	0.03285	1.93204	2.05405	1.9320	2.05405	1.9287	2.0542	Ref: N.B.Ishwar and B.L.Jha.[49]
1	0.09805	1.89310	2.10535	1.8970	2.1163	1.8873	2.1056	
2	0.16258	1.86786	2.14300	1.8731	2.1588	1.8601	2.1430	
3	0.22644	1.84823	2.17528	1.8537	2.1930	1.8387	2.1749	
4	0.28962	1.83186	2.20435	1.8372	2.2224	1.8208	2.2036	m+ = 0.0054378615
5	0.35212	1.81769	2.23133	1.8225	2.2484	1.8051	2.2302	c+ = 2.68992173
6	0.41395	1.80512	2.25683	1.8092	2.2719	1.7912	2.2555	m− = 0.0096879645
7	0.47511	1.79378	2.28121	1.7969	2.2935	1.7785	2.2800	c− = 2.6814423
8	0.53559	1.78343	2.30473	1.7856	2.3135	1.7670	2.3036	
9	0.5940	1.77389	2.32757	1.7750	2.3323	1.7462	2.3268	
10	0.65453	1.76503	2.34985	1.7650	2.34985	1.7562	2.3498	

TABLE 3.3a

Classical Turning Points of X State of HoF

V	U(r) cm^{-1}	RKRV Method r_{min} (A°)	r_{max}(A°)	Rapid Method r_{min} (A°)	r_{max}(A°)	Using Functional Relation r_{min} (A°)	r_{max}(A°)	Constants and
0	0.03806	1.88570	1.99948	1.8833	1.9915	1.9520	2.0803	Ref: N.B.Ishwar and B.L.Jha[49]
1	0.11370	1.84900	2.04669	1.8501	2.0477	1.9109	2.1353	
2	0.18870	1.82525	2.08120	1.8273	2.0861	1.8841	2.1767	
3	0.26305	1.80640	2.11053	1.8090	2.1170	1.8632	2.2132	
4	0.33675	1.79100	2.13689	1.7932	2.1436	1.8456	2.2475	
5	0.40981	1.77747	2.16216	1.7792	2.1672	1.8304	2.2807	m+ = 0.0057538500
6	0.48222	1.76544	2.18421	1.7665	2.1886	1.8168	2.3140	c+ = 2.778057599
7	0.55399	1.75457	2.20608	1.7548	2.2083	1.8045	2.3480	m− = 0.0097503204
8	0.62511	1.74400	2.22711	1.7440	2.2265	1.7932	2.3840	c− = 2.770265733
9	0.69559	1.73500	2.24750	1.7337	2.2436	1.7828	2.4234	
10	0.76542	1.72693	2.26725	1.7241	2.2597	1.7731	2.4698	

TABLE 3.3b

Classical Turning Points of A State of HoF

V	U(r) cm $^{-1}$	RKRV Method r_{min} (A°)	r_{max}(A°)	Rapid Method r_{min} (A°)	r_{max}(A°)	Using Functional Relation r_{min} (A°)	r_{max}(A°)	Constants and References
0	0.03347	1.94941	2.07098	1.9466	2.0559	1.9612	2.0854	Ref: N.B.Ishwar B.L.Jha[49]
1	0.09926	1.91201	2.12404	1.9134	2.1251	1.9212	2.1369	
2	0.16397	1.88813	2.16377	1.8908	2.1722	1.8951	2.1922	
3	0.22755	1.86975	2.19821	1.8726	2.2099	1.8747	2.2073	
4	0.29012	1.85455	2.22968	1.8571	2.2421	1.8577	2.2368	
5	0.35156	1.84149	2.25924	1.8434	2.2705	1.8430	2.2645	m+ = 0.0043414036
6	0.41191	1.82996	2.28749	1.8311	2.2960	1.82996	2.2910	c+ = 2.780563306
7	0.47117	1.81960	2.31479	1.8198	2.3193	1.8182	2.3168	m− = 0.0090557363
8	0.52935	1.81018	2.34139	1.8094	2.3408	1.8075	2.3422	c− = 2.77102786
9	0.58644	1.80152	2.36749	1.7998	2.3608	1.7977	2.3676	
10	0.64243	1.79347	2.39322	1.7908	2.3894	1.7886	2.3932	

TABLE 3.4

Classical Turning Points of LuF Molecule

V	U(r)		RKRV Method		Rapid Method		Using Functional Relation		Constants and References
	$U(r_{min})$ cm^{-1}	$U(r_{max})$ cm^{-1}	r_{min}(A°)	r_{min}(A°)	r_{min}(A°)	r_{max}(A°)	r_{min}(A°)	r_{max}(A°)	
0	503.78	312.34	1.8626	1.9762	1.8626	1.9762	1.8573	1.9805	Ref: R.R.Reddy & A.S.R.Reddy.[50]
1	913.03	927.05	1.8261	2.0236	1.8426	2.0345	1.8342	2.0236	
2	1518.07	1534.62	1.8025	2.0582	1.8188	2.0724	1.8081	2.0552	
3	2118.67	2135.36	1.7840	2.0770	1.7986	2.1019	1.7869	2.0827	
4	2714.48	2729.56	1.7686	2.1142	1.7805	2.1266	1.7686	2.1082	m+ = 0.4409242711
5	3305.44	3317.19	1.7553	2.1387	1.7637	2.1479	1.7521	2.1329	c+ = 1.953501704
6	3891.38	3898.33	1.7435	2.1618	1.7479	2.1668	1.7371	2.1578	m− = 1.017146801
7	4472.29	4472.85	1.7328	2.1839	1.7328	2.1839	1.7230	2.1839	c− = 0.8380547195

TABLE 3.5

Classical Turning Points of SiTe Molecule

V	U(r): $U(r_{min})$ cm^{-1}	U(r): $U(r_{max})$ cm^{-1}	RKRV Method: r_{min} (A°)	RKRV Method: r_{max} (A°)	Rapid Method: r_{min} (A°)	Rapid Method: r_{max} (A°)	Using Functional Relation: r_{min} (A°)	Using Functional Relation: r_{max} (A°)	Constants and References
0	247.75	236.26	2.2187	2.3286	2.2146	2.3226	2.2273	2.3339	Ref: R.R.Reddy and A.S.R.Reddy[50]
1	733.53	713.98	2.1818	2.3735	2.1841	2.3764	2.1898	2.3758	
2	1194.55	1190.37	2.1579	2.4060	2.1629	2.4119	2.1652	2.4060	
3	1692.27	1664.69	2.1391	2.4334	2.1435	2.4398	2.1435	2.4317	
4	2166.13	2136.75	2.1234	2.4578	2.1269	2.4632	2.1257	2.4551	
5	2636.44	2623.85	2.1097	2.4802	2.1118	2.4844	2.1097	2.4779	m+ = 0.3945040005
6	3103.25	3073.72	2.0974	2.5011	2.0977	2.5020	2.0952	2.4983	c+ = 1.796591126
7	3566.58	3538.49	2.0863	2.5210	2.0843	2.5187	2.0817	2.5191	m− = 0.8500464282
8	4026.77	4000.79	2.0762	2.5400	2.0715	2.5338	2.0690	2.5400	c− = 0.7661096108

TABLE 3.6

Classical Turning Points of PtD Molecule

V	U(r) cm^{-1}	RKRV Method		Lakshman&Rao's Method		Rapid Method		Using Functional Relation		Constants and References
		r_{min} (A°)	r_{max}(A°)	r_{min} (A°)	r_{max}(A°)	r_{min} (A°)	r_{max}(A°)	r_{min} (A°)	r_{max}(A°)	
					$A^2\Delta_{5/2}$ State					
0	592.75	1.5910	1.8311	1.5913	1.8309	1.5883	1.8178	1.6411	1.8622	m_+ = 0.2262646692
1	1737.75	1.5308	1.9530	1.5302	1.9534	1.5398	1.9801	1.5644	1.9530	c_+ = 2.862355426
2	2828.75	1.4951	2.0520	1.4950	2.0526	1.5038	2.0815	1.5121	2.0232	m_- = 1.12232333
3	3865.75	1.4706	2.1447	1.4703	2.1442	1.4772	2.1569	1.4706	2.0859	c_- = 1.366886058
4	4848.75	1.4519	2.2334	1.4517	2.2331	1.4459	2.2172	1.4349	2.1624	
5	5777.75	1.4375	2.3213	1.4372	2.3316	1.4208	2.2673	1.4035	2.3050	
					$B^2\Delta_{5/2}$ State					
0	595.65	1.5615	1.8010	1.5612	1.8007	1.5598	1.7834	1.6004	1.8304	m_+ = 0.2076140321
1	1726.35	1.4980	1.9244	1.4976	1.9248	1.5040	1.9589	1.5221	1.9244	c_+ = 2.903530721
2	2776.25	1.4585	2.0277	1.4587	2.0279	1.4637	2.0656	1.4702	1.9961	m_- = 0.9665303286
3	3745.35	1.4295	2.1261	1.4292	2.1258	1.4303	2.1435	1.4295	2.0626	c_- = 1.641771103
4	4633.65	1.4048	2.2242	1.4046	2.2237	1.4014	2.2044	1.3958	2.1337	
5	5441.15	1.3825	2.3250	1.3828	2.3248	1.3759	2.2536	1.3671	2.2460	
					$X^2\Delta_{5/2}$ State					
0	837.75	1.4311	1.6318	1.4308	1.6320	1.4283	1.6254	1.4653	1.6504	m_+ = 0.3763936243
1	2481.75	1.3720	1.7243	1.3723	1.7245	1.3810	1.7398	1.3974	1.7243	c_+ = 2.671935232
2	4081.75	1.3361	1.7959	1.3357	1.7954	1.3442	1.8110	1.3493	1.7810	m_- = 1.453580204
3	5643.75	1.3088	1.8580	1.3083	1.8582	1.3112	1.8647	1.3088	1.8342	c_- = 1.059547045
4	7161.75	1.2855	1.9170	1.2859	1.9167	1.2802	1.9084	1.2727	1.9004	
5	8637.75	1.2677	1.9724	1.2672	1.9726	1.2501	1.9452	1.2392	1.9724	Ref: Ram Samujh Ram, S.B.Rai and K.N.Upadhya.[51]

TABLE 3.7

Classical Turning Points for PtH Molecule

V	U(r) cm^{-1}	RKRV Method r_{min} (A°)	RKRV Method r_{max}(A°)	Lakshman&Rao's Method r_{min} (A°)	Lakshman&Rao's Method r_{max}(A°)	Rapid Method r_{min} (A°)	Rapid Method r_{max}(A°)	Using Functional Relation r_{min} (A°)	Using Functional Relation r_{max}(A°)	Constants and References
					$A^2\Delta_{5/2}$ State					
0	830.86	1.6000	1.8866	1.6003	1.8863	1.596	1.866	1.656	1.926	
1	2409.80	1.5340	2.0338	1.5343	2.0341	1.533	2.075	1.560	2.0338	
2	3878.36	1.4785	2.1572	1.4780	2.1568	1.486	2.202	1.495	2.115	m+ = 0.2016334763
3	5236.54	1.4430	2.2735	1.4431	2.2731	1.446	2.294	1.443	2.190	c+ = 3.052903678
4	6484.34	1.4148	2.3891	1.4142	2.3894	1.4111	2.365	1.399	2.268	m− = 1.079311185
5	7621.76	1.3885	2.5089	1.3892	2.5093	1.379	2.423	1.360	2.3830	c− = 1.557319837
					$B^2\Delta_{5/2}$ State					
0	834.50	1.5503	1.8360	1.5500	1.8361	1.551	1.8019	1.6068	1.8884	
1	2380.50	1.4775	1.9950	1.4772	1.9949	1.4869	2.0489	1.5118	1.9950	
2	3762.50	1.4319	2.1341	1.4324	2.1337	1.4378	2.2036	1.4448	2.0779	m+ = 0.1640918454
3	4980.50	1.3970	2.2733	1.3972	2.2727	1.4006	2.3075	1.3970	2.1470	c+ = 3.133502654
4	6034.50	1.3663	2.4203	1.3659	2.4207	1.3671	2.3849	1.3559	2.2122	m− = 1.010484405
5	6824.50	1.3355	2.5861	1.3350	2.5857	1.3433	2.4372	1.3275	2.2710	c− = 1.712307491
					$X^2\Delta_{5/2}$ State					
0	1178.00	1.4199	1.6600	1.4203	1.6598	1.4149	1.6493	1.4760	1.6912	
1	3471.00	1.3539	1.7750	1.3535	1.7747	1.3649	1.7983	1.3941	1.7750	
2	5680.00	1.3125	1.8650	1.3128	1.8653	1.3247	1.8893	1.3347	1.8390	m+ = 0.3326228563
3	7805.00	1.2838	1.9775	1.2828	1.9471	1.2877	1.9563	1.2838	1.8992	c+ = 2.892327269
4	9846.00	1.2590	2.0245	1.2588	2.0249	1.2517	2.0108	1.2372	1.9653	m− = 1.745835631
5	11803.00	1.2390	2.1010	1.2387	2.1006	1.2157	2.0559	1.1930	2.1010	c− = 0.7918846636
										Ref: Ram Samujh Ram, S.B.Rai and K.N.Upadhya.[51]

TABLE 3.8a

Classical Turning Points of $A^3\Pi_0$ State of InBr

V	U(r) cm^{-1}	RKRV Method r_{min} (A°)	 r_{max}(A°)	Rapid Method r_{min} (A°)	 r_{max}(A°)	Using Functional Relation r_{min} (A°)	 r_{max}(A°)	Constants and References
0	113.65	2.4321	2.5448	2.4321	2.5448	2.4321	2.5181	1. Singh, V.B., Rai, A.K. Rai, S.B. & Rai, D.K.[52]
1	339.29	2.3952	2.5913	2.4057	2.6115	2.4005	2.5507	2. Vempti, S.N. & Jones, W.E.[53]
2	562.50	2.3709	2.6252	2.3860	2.6543	2.3785	2.5741	3. Singh, V.B. *et al.*[54]
3	783.20	2.3518	2.6541	2.3690	2.6874	2.3603	2.5940	4. Singh, V.B. *et al.*[55]
4	1001.30	2.3356	2.6801	2.3534	2.7148	2.3443	2.6119	m+ = 0.481747246
5	1216.69	2.3214	2.7042	2.3388	2.7384	2.3298	2.6289	c+ = 1.179226072
6	1429.31	2.3086	2.7270	2.3248	2.7592	2.3163	2.6452	m− = 1.683705322
7	1639.04	2.2969	2.7488	2.3114	2.7778	2.3037	2.6614	c− = 1.792609947
8	1845.79	2.2860	2.7699	2.2983	2.7947	2.2917	2.6779	
9	2049.52	2.2757	2.7905	2.2854	2.8102	2.2801	2.6950	
10	2250.10	2.2660	2.8104	2.2727	2.8244	2.2690	2.7136	
11	2447.54	2.2568	2.8304	2.2602	2.8377	2.2583	2.7350	
12	2642.06	2.2478	2.8500	2.2478	2.8500	2.2478	2.7637	

TABLE 3.8b

Classical Turning Points of $X^1\Sigma^+$ State of InBr

V	U(r) cm	RKRV Method		Rapid Method		Using Functional Relation		Constants and References
		r_{min} (A°)	r_{max}(A°)	r_{min} (A°)	r_{max}(A°)	r_{min} (A°)	r_{max}(A°)	
0	111.36	2.4807	2.6026	2.4680	2.6026	2.5022	2.6026	1. Singh V.B. <u>et al</u>.[52]
1	333.26	2.4510	2.6486	2.4426	2.6623	2.4666	2.6417	2. Vempti, S.N. and Jones, W.E.[53]
2	554.08	2.4262	2.6818	2.4241	2.7016	2.4423	2.6700	3. Singh, V.B. <u>et al</u>.[54]
3	773.82	2.4067	2.7098	2.4085	2.7325	2.4227	2.6940	4. Singh V.B. <u>et al</u>.[55]
4	992.49	2.3903	2.7346	2.3946	2.7584	2.4054	2.7157	m+ = 0.369876922
5	1210.08	2.3760	2.7574	2.3818	2.7811	2.3901	2.7360	c+ = 1.413964051
6	1426.59	2.3632	2.7788	2.3698	2.8013	2.3761	2.7556	m− = 1.070874176
7	1642.04	2.3517	2.7989	2.3584	2.8196	2.3630	2.7748	c− = −0.3333742625
8	1856.40	2.3410	2.8182	2.3475	2.8365	2.3508	2.7940	
9	2069.67	2.3312	2.8367	2.3370	2.8521	2.3392	2.8134	
10	2281.86	2.3220	2.8545	2.3268	2.8666	2.3282	2.8335	
11	2492.96	2.3134	2.8719	2.3168	2.8802	2.3176	2.8549	
12	2703.01	2.3053	2.888	2.3071	2.8931	2.3074	2.8782	
13	2911.95	2.2976	2.9053	2.2976	2.9053	2.2976	2.9053	

TABLE 3.8c

Classical Turning Points $B^2\Pi$ State of InBr

V	U(r) cm -1	RKRV Method		Rapid Method		Using Functional Relation		Constants and References
		r_{min} (A°)	r_{max}(A°)	r_{min} (A°)	r_{max}(A°)	r_{min} (A°)	r_{max}(A°)	
0	111.75	2.4303	2.5440	2.4303	2.4544	2.4498	2.5440	1. Singh, V.B. _et al._[52]
1	333.45	2.3935	2.5913	2.4042	2.6138	2.4151	2.5798	2. Vempti, S.N. and Jones, W.E.[53]
2	552.50	2.3693	2.6260	2.3847	2.6586	2.3908	2.6055	3. Singh, V.B. _et al._[54]
3	768.83	2.3503	2.6556	2.3677	2.6931	2.3707	2.6274	4. Singh, V.B. _et al._[55]
4	982.25	2.3842	2.6824	2.3522	2.7216	2.3531	2.6472	m+ + 0.4749714633
5	1192.68	2.3201	2.7073	2.3376	2.7461	2.3371	2.6659	c+ = 1.181092513
6	1399.93	2.3074	2.7310	2.3226	2.7676	2.3222	2.6841	m- = 1.781170524
7	1603.87	2.2958	2.7537	2.3101	2.7868	2.3082	2.7022	c- = -2.046254552
8	1804.37	2.2849	2.7758	2.2970	2.8043	2.2949	2.7207	
9	2001.29	2.2746	2.7974	2.2841	2.8201	2.2821	2.7403	
10	2194.60	2.2649	2.8187	2.2714	2.8348	2.2699	2.7621	
11	2384.05	2.2555	2.8398	2.2589	2.8482	2.2580	2.7887	
12	2570.00	2.2464	2.8608	2.2464	2.8608	2.2464	2.8403	

TABLE 3.9a

α_e and $\omega_e x_e$ in (cm^{-1}) using MRK Potential

Molecule	α_e (experimental)	α_e (calculated)	Percentage Error	$\omega_e x_e$ (experimental)	$\omega_e x_e$ (calculated)	Percentage error
AlBr	0.000853	0.000401	52.90%	1.28	0.4768	62.75%
AlCl	0.002	0.000730	63.50%	1.95	0.7310	62.50%
BBr	0.0035	0.00210	40.00%	3.52	1.480	57.905
BCl	0.00646	0.00334	48.20%	5.11	2.051	59.90%
BeF	0.01685	0.01049	37.70%	9.12	4.46	51.10%
BrF	0.005214	0.00141	72.90%	3.00	1.067	64.40%
ClF	0.004358	0.00202	53.60%	9.90	1.55	34.30%
ICl	0.00536	0.00203	62.10%	1.465	0.342	76.60%
InBr				0.65	0.161	75.20%
KBr				0.70	0.223	68.10%
MnH	0.16079	0.13006	19.00%		17.047	
NiH	0.248	0.19052	23.20%		23.477	
PbH	0.144	0.09472	34.20%	29.75	14.889	49.96%
PO	0.0055	0.002823	48.60%	6.52	2.283	64.98%
GeO	0.0029	0.00135	53.40%	4.30	1.411	67.19%
MgO	0.0050	0.00252	49.60%	5.10	1.721	66.25%

TABLE 3.9b

Comparison with Different Potentials

Potential Used	Average Percentage Error in α_e	Average Percentage Error in $\omega_e x_e$
Morse	±25.98	±26.82
Rydberg	±22.39	±19.92
MR Potential	±26.54	±24.48
RK Potential	±26.12	±22.62
MK Potential	±20.43	±20.13
MRK Potential	±47.10	±65.00

TABLE 3.10

Extended Rydberg Potential Energy Curve for $X^2\Sigma$ State of YbF

V	G(v)	r_{min}	r_{max}	U using relation (3.32) U_{min}	 U_{max}	Average U
0	250.40	1.95657	2.08154	220.95	245.99	233.47
1	747.90	1.91658	2.13381	740.45	745.35	744.90
2	1240.99375	1.89064	2.17211	1235.85	1240.00	1237.925
3	1729.67375	1.870247	2.20474	1699.98	1745.00	1722.79
4	2213.94375	1.85366	2.23412	2195.99	2200.671	2198.3305
5	2893.80375	1.83900	2.26132	2890.92	2779.68	2835.3
6	3169.2540	1.82624	2.28692	3190.25	3180.35	3185.30
7	3640.0125	1.81464	2.31144	3630.27	3650.15	3640.21
8	4106.92375	1.80406	2.33499	4108.98	4107.25	4108.115
9	4169.14375	1.79430	2.35781	4570.43	4568.34	4569.385
10	5026.95375	1.78450	2.38002	5023.90	5027.85	5025.875

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TABLE 3.11

Extended Rydberg Potential Energy Curve for X State of HoF Molecule

V	G(v)	r_{min}	r_{max}	U using relation (3.32) U_{min}	 U_{max}	Average U
0	306.99	1.88570	1.99948	303.25	304.3	303.775
1	917.07	1.84900	2.04669	889.75	910.15	899.95
2	1521.95	1.82525	2.08120	1500.00	1519.90	1509.95
3	2121.63	1.80642	2.11053	2105.65	2136.50	2121.075
4	2716.11	1.79100	2.13689	2610.95	2700.55	2655.75
5	3305.39	1.77747	2.16128	3395.40	3295.73	3345.565
6	3889.47	1.76544	2.18421	3789.98	3895.37	3842.675
7	4468.35	1.75457	2.20608	4569.40	4420.55	4494.975
8	5042.03	1.74400	2.22711	5000.45	5030.95	5015.7
9	5610.51	1.73500	2.24750	5590.35	5615.85	5603.1
10	6173.79	1.72693	2.26725	6150.70	6160.95	6153.825

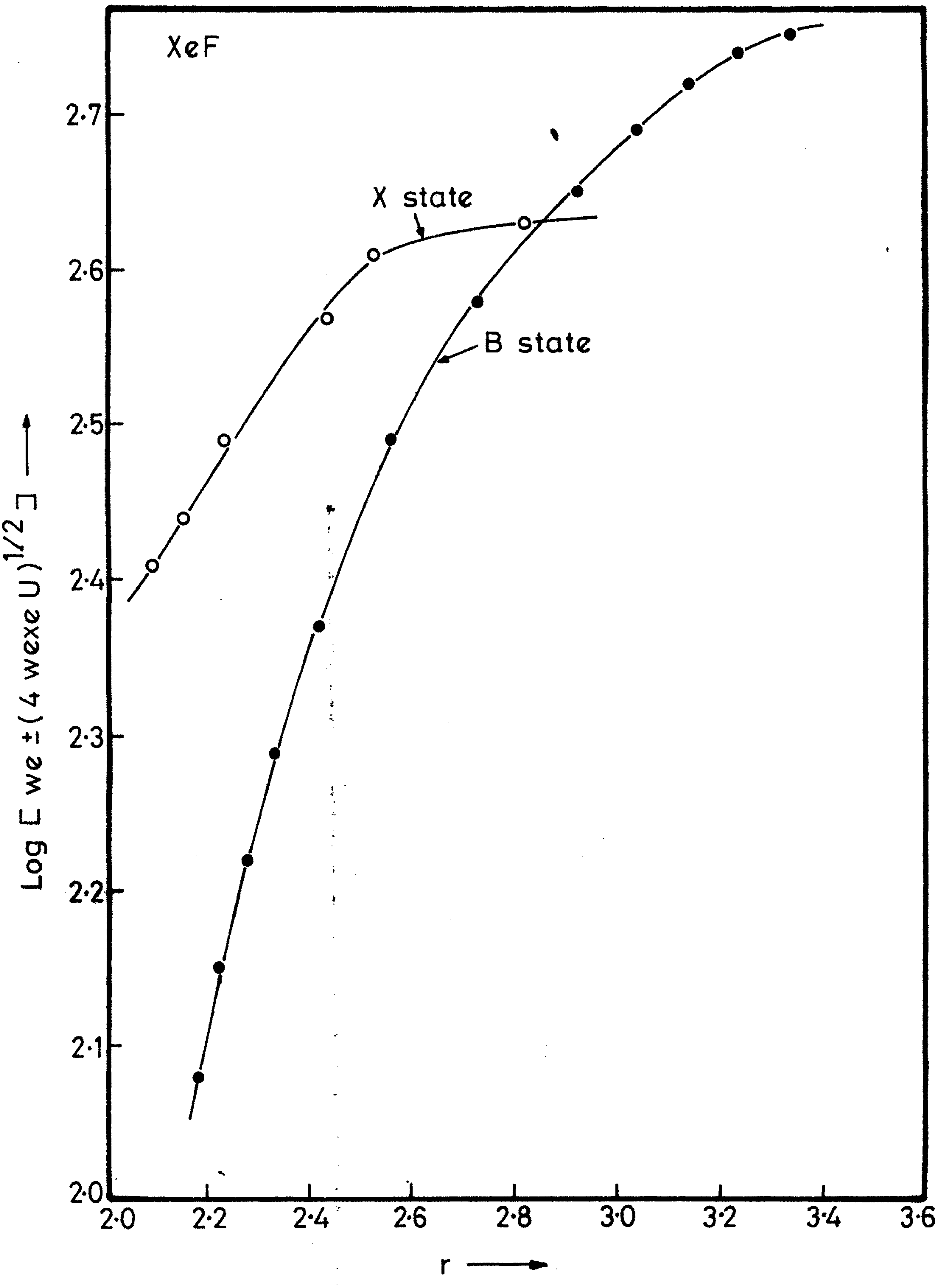
XeF
X state
B state
Log [we ± (4 wexe U)^1/2] ⟶
2·0
2·1
2·2
2·3
2·4
2·5
2·6
2·7
2·0
2·2
2·4
2·6
2·8
3·0
3·2
3·4
3·6
r ⟶

Fig. 3·1

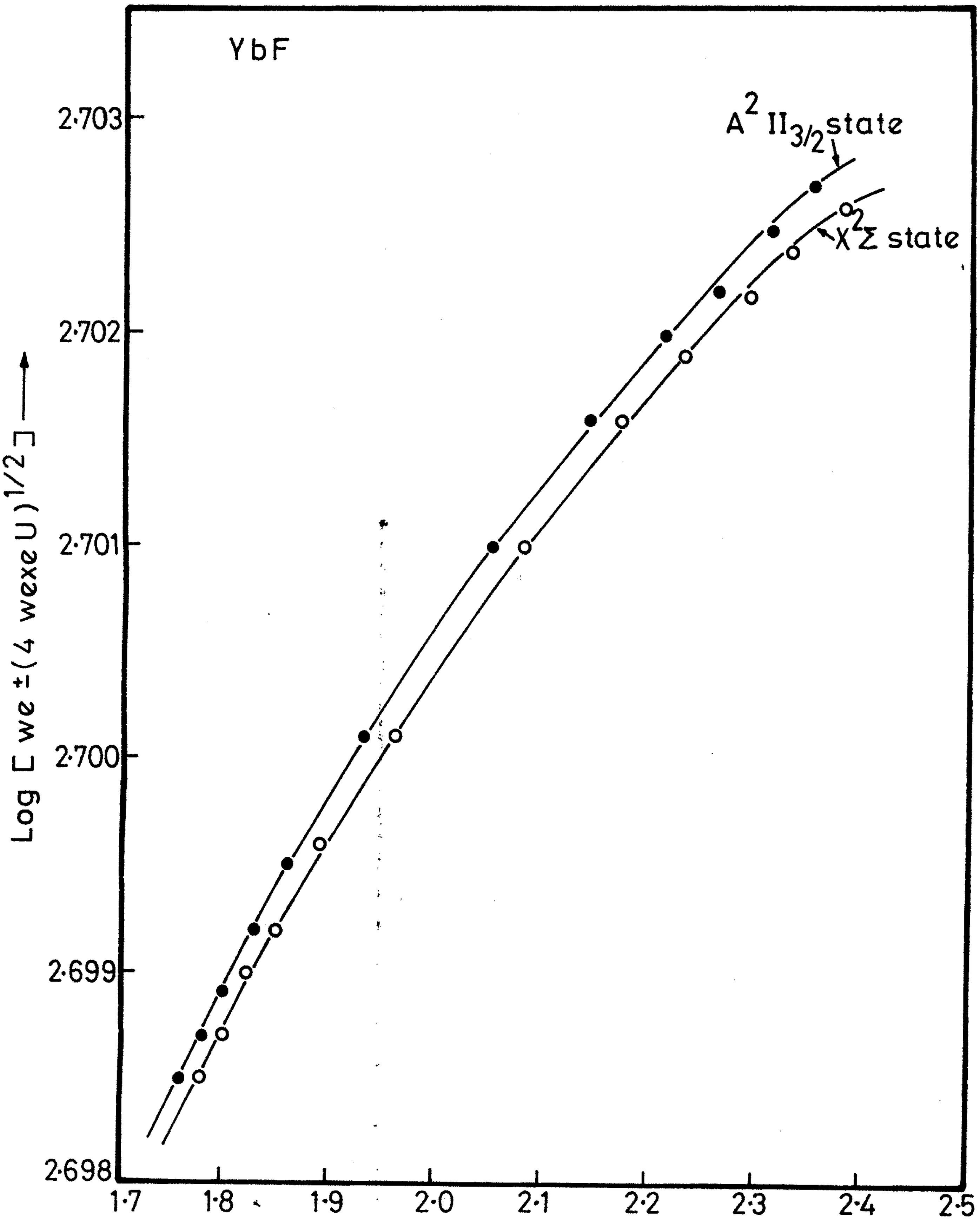
YbF
$A^2\Pi_{3/2}$ state
$X^2\Sigma$ state
Log [we ±(4 wexe U)$^{1/2}$]
2·703
2·702
2·701
2·700
2·699
2·698
1·7
1·8
1·9
2·0
2·1
2·2
2·3
2·4
2·5
r

Fig. 3·2

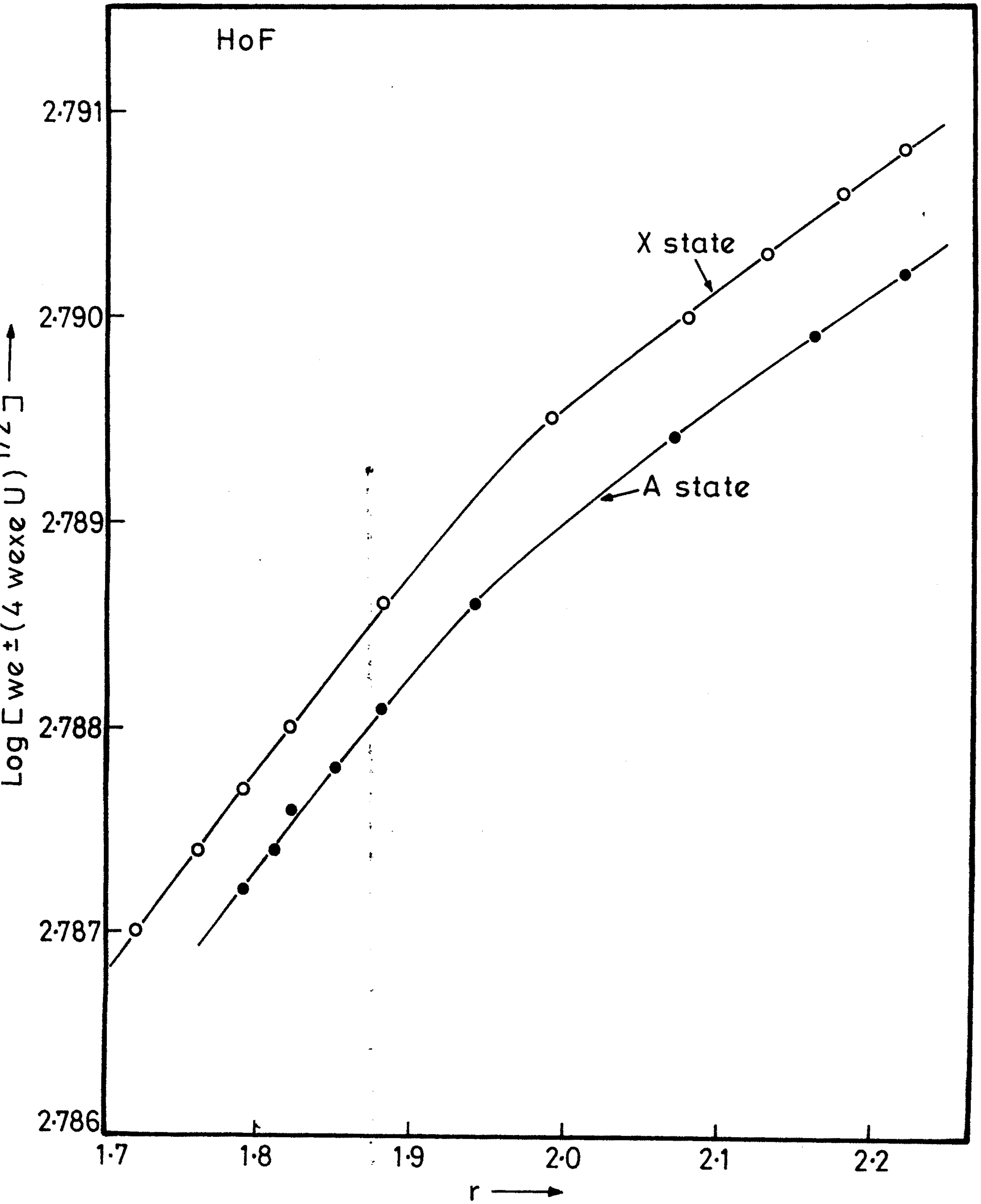
HoF
X state
A state
Log [we ± (4 wexe U)]^1/2 ⟶
2·791
2·790
2·789
2·788
2·787
2·786
1·7
1·8
1·9
2·0
2·1
2·2
r ⟶

Fig. 3·3

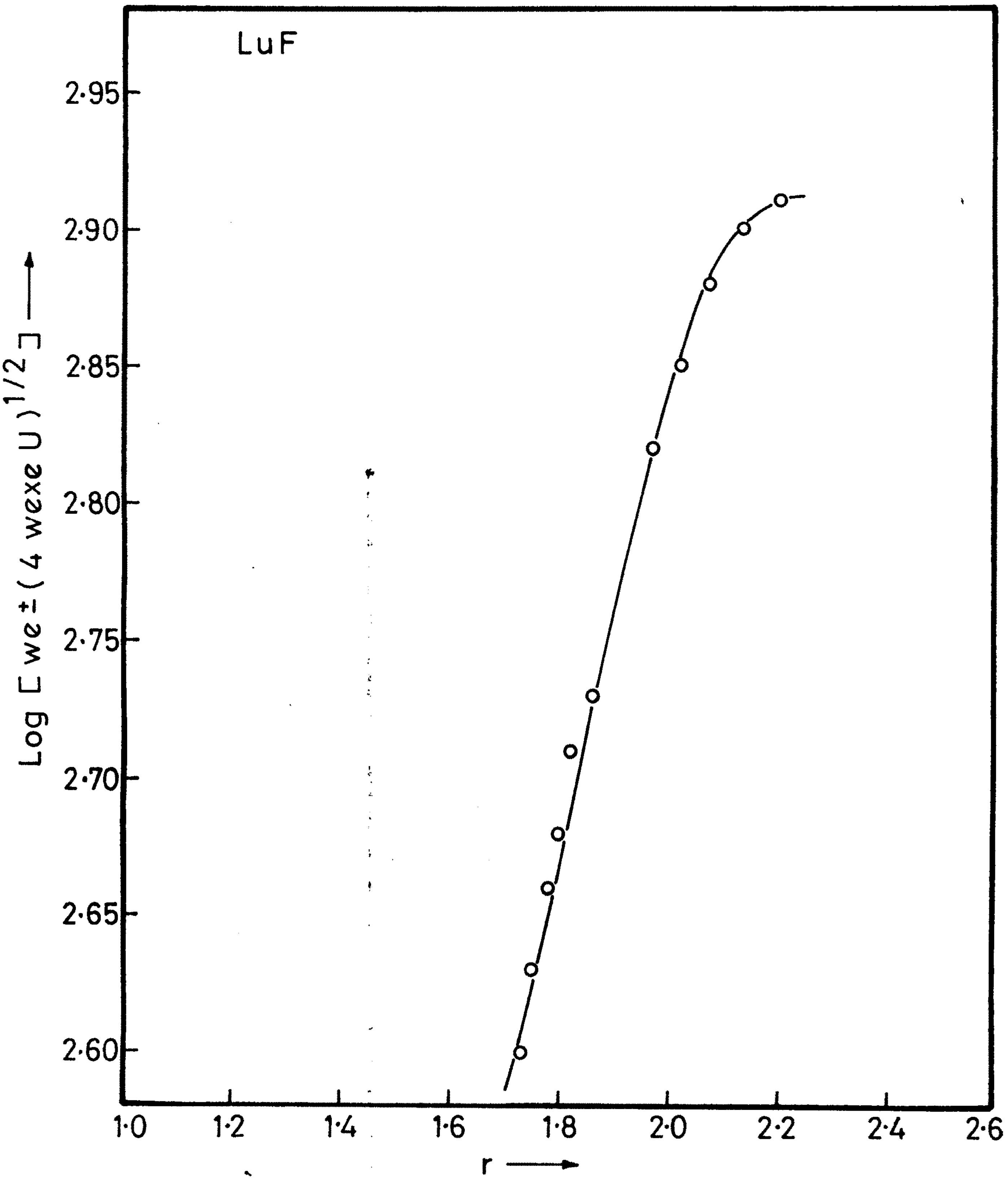
LuF
2·95
2·90
2·85
2·80
2·75
2·70
2·65
2·60
Log [we ± (4 wexe U)^{1/2}]
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
2·6
r

Fig. 3·4

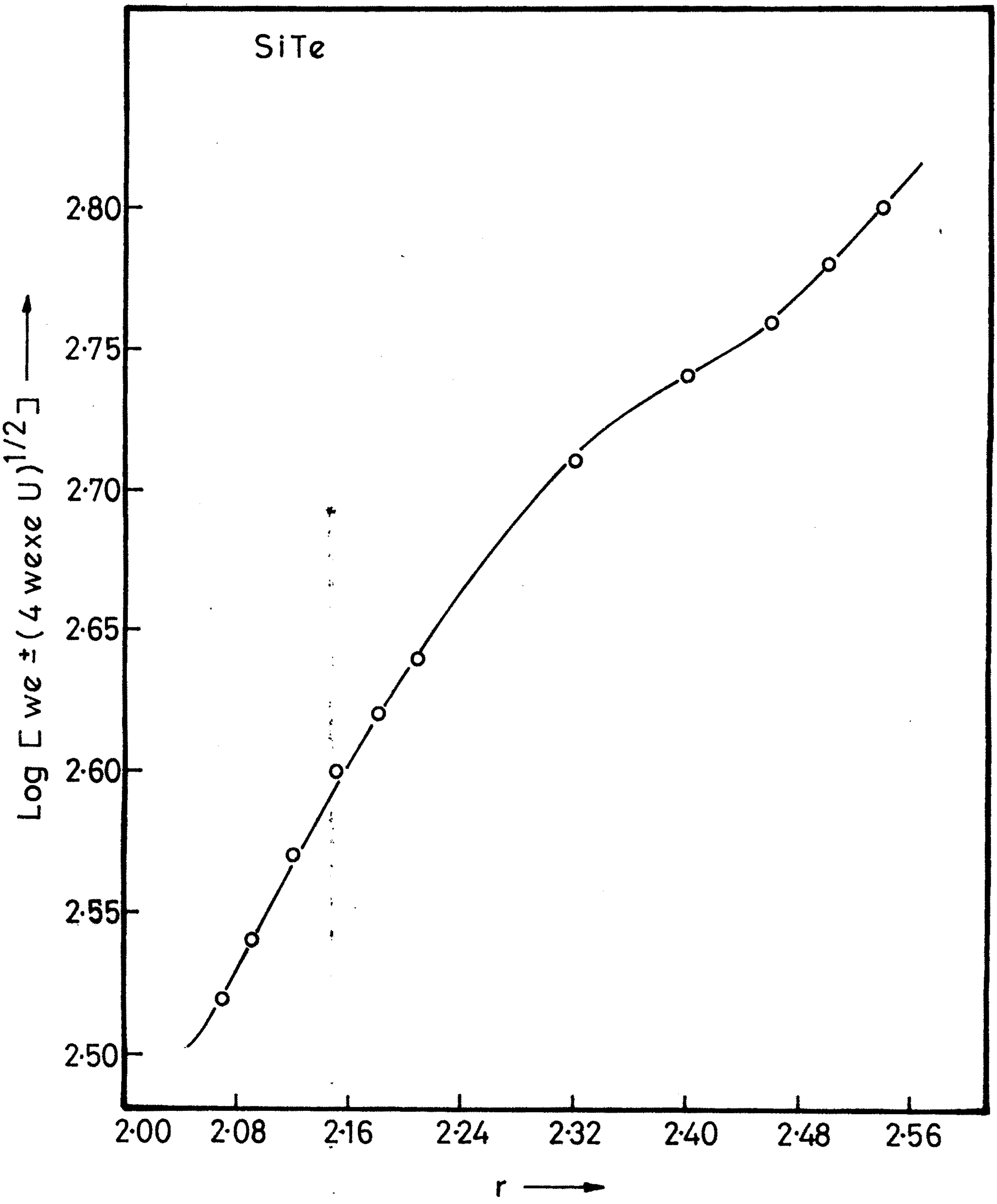
SiTe
Log [we ± (4 wexe U)$^{1/2}$]
2·50
2·55
2·60
2·65
2·70
2·75
2·80
2·00
2·08
2·16
2·24
2·32
2·40
2·48
2·56
r

Fig. 3·5

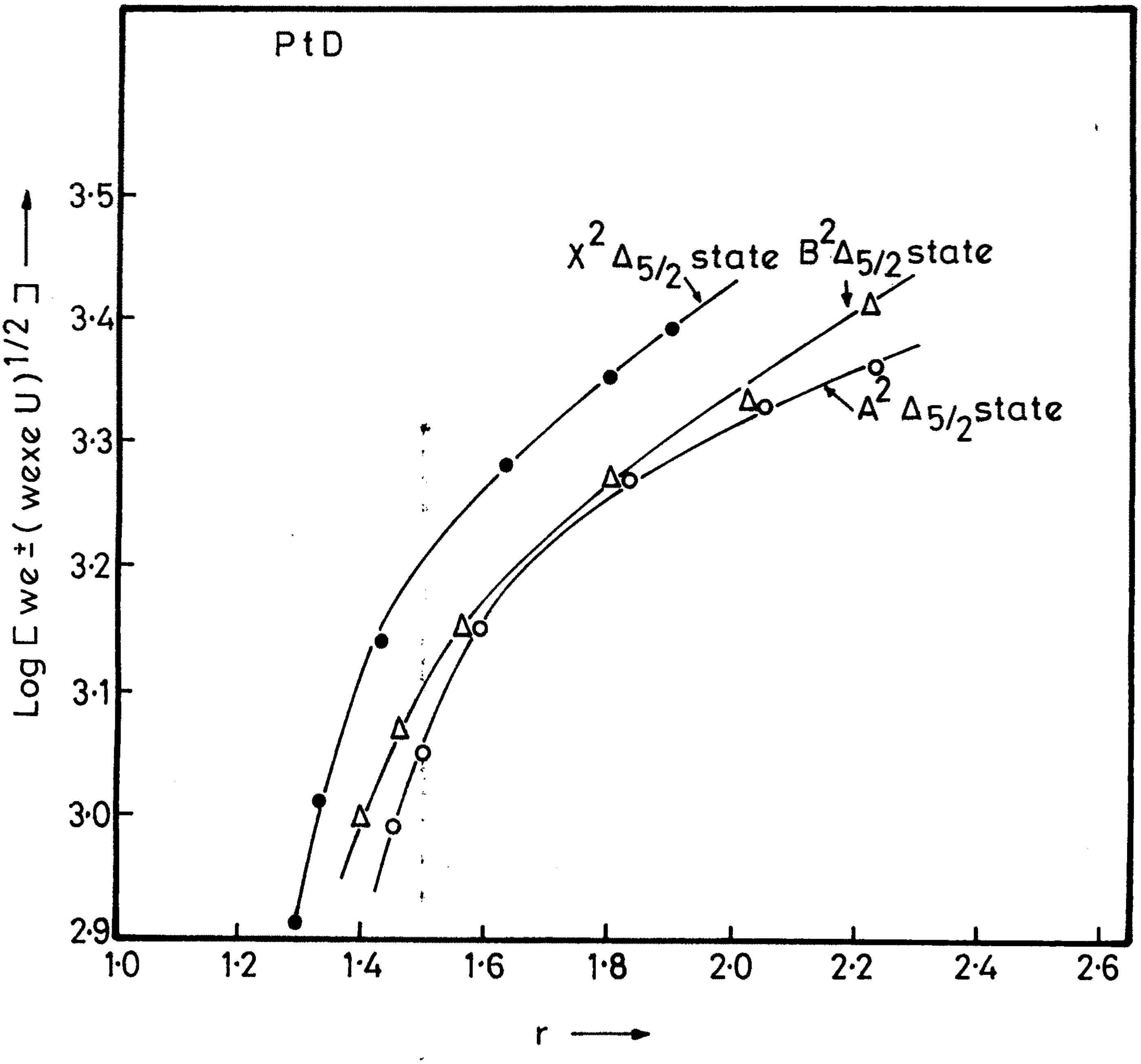
PtD
Log [we ± (wexe U)$^{1/2}$] ⟶
3·5
3·4
3·3
3·2
3·1
3·0
2·9
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
2·6
r ⟶
$X^2\Delta_{5/2}$ state
$B^2\Delta_{5/2}$ state
$A^2\Delta_{5/2}$ state

Fig. 3·6

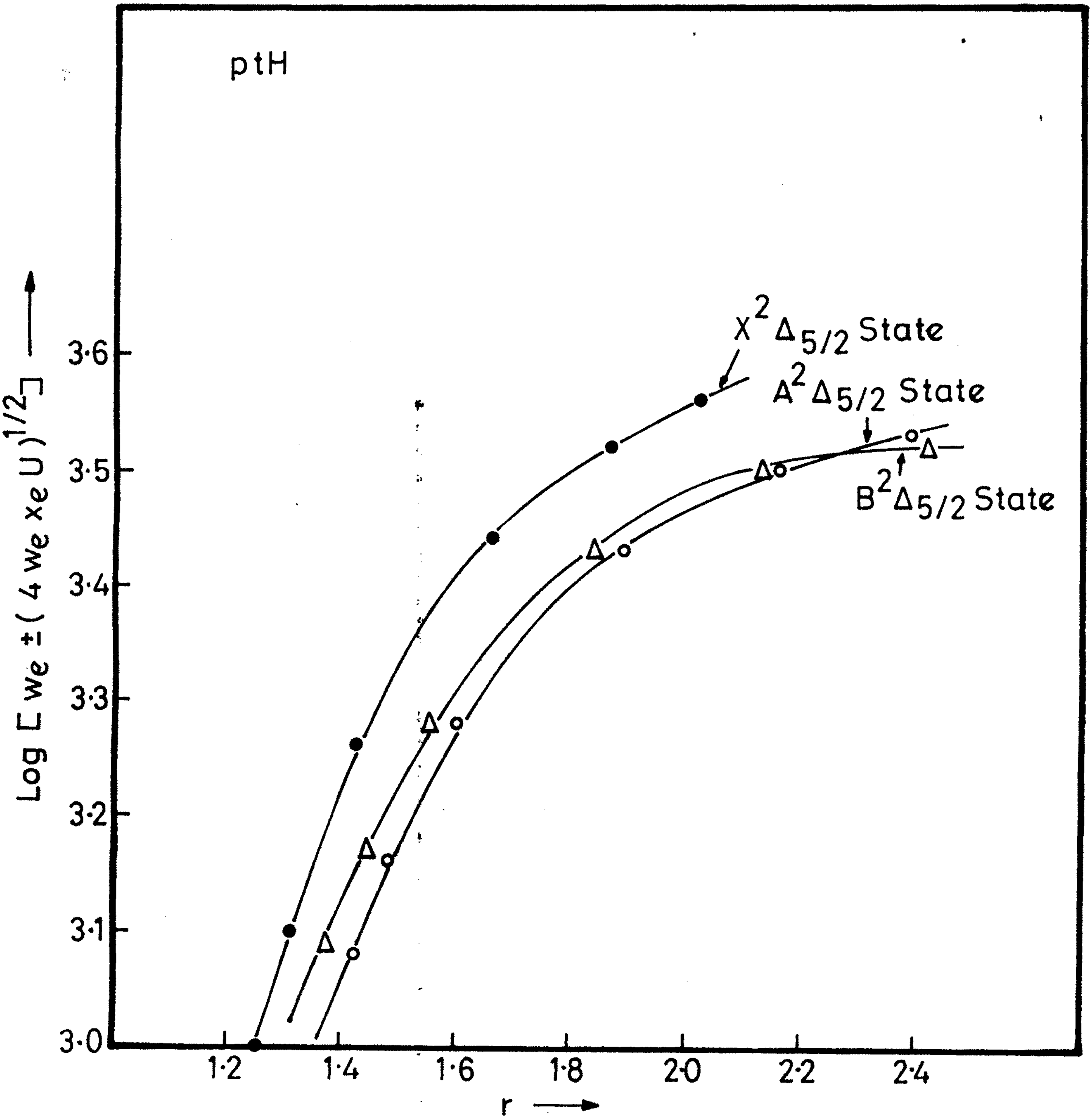
ptH
$X^2\Delta_{5/2}$ State
$A^2\Delta_{5/2}$ State
$B^2\Delta_{5/2}$ State
Log [we ± (4 we xe U)^1/2]
3·0
3·1
3·2
3·3
3·4
3·5
3·6
1·2
1·4
1·6
1·8
2·0
2·2
2·4
r

Fig. 3·7

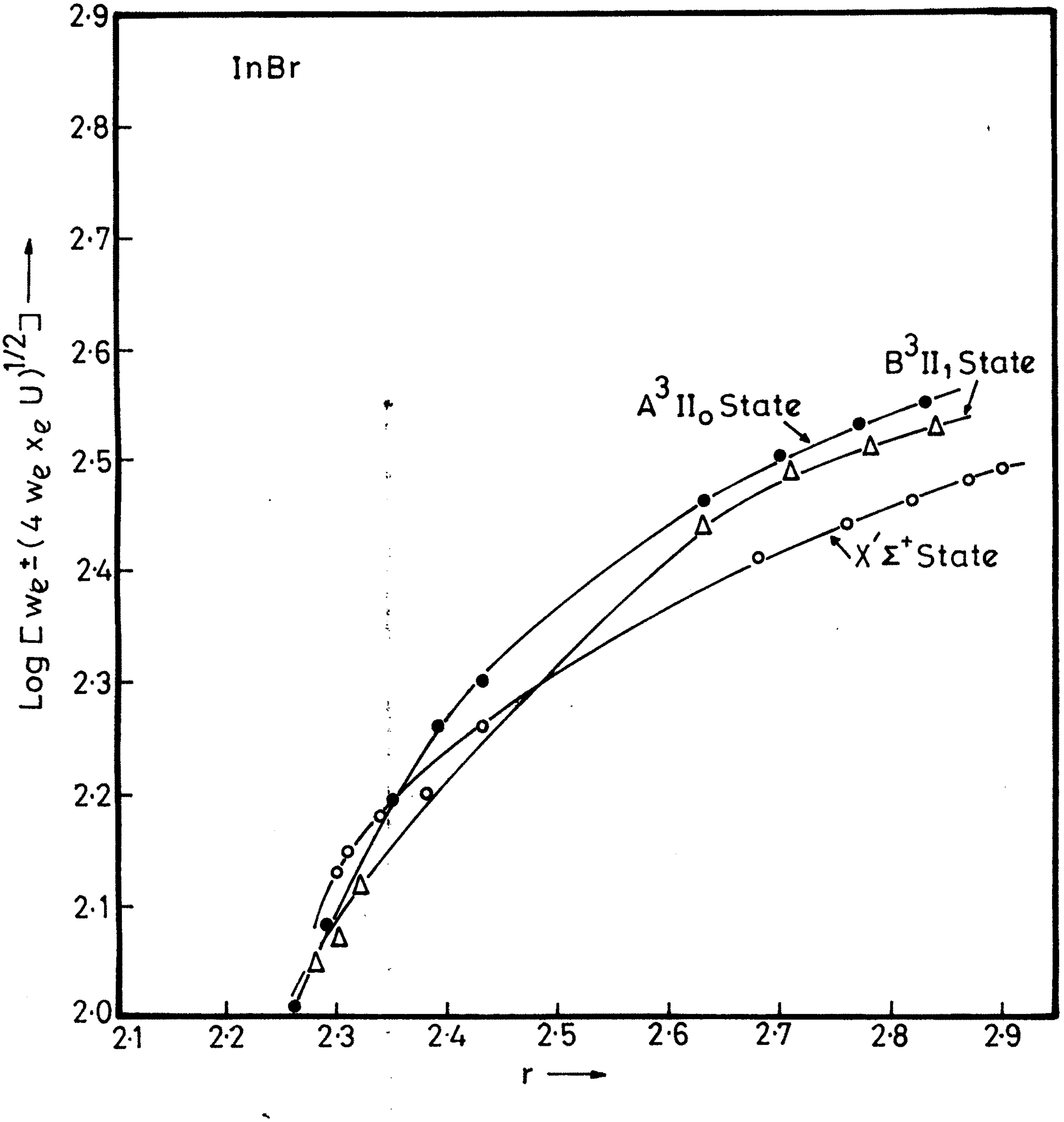
InBr
A$^3\Pi_0$ State
B$^3\Pi_1$ State
X$^1\Sigma^+$ State
Log [we ± (4 we xe U)$^{1/2}$] →
r →
2·0
2·1
2·2
2·3
2·4
2·5
2·6
2·7
2·8
2·9

Fig. 3·8