Chapter -I

INTRODUCTION

CHAPTER - I / INTRODUCTION

1.1 Historical:

1.1.1 The Role of Molecular Spectroscopy:

Spectroscopy is the study of interaction of radiation with matter. Spectroscopy is one of the most powerful tools for the study of atomic and molecular structure.[1] With the help of spectroscopic techniques, the measurements of radiation frequency are made experimentally and the energy levels are deduced from these measurements. The various branches of spectroscopy generally involve the measurements of two parameters, i.e. energy of radiation emitted or absorbed by the system and the intensity of spectral line.

I) Atomic Spectroscopy : It deals with the interaction of electromagnetic radiation with atoms which are most commonly in their lowest energy state called 'ground state'.

II) Molecular Spectroscopy : It deals with the interaction of electromagnetic radiation with molecules. In case of molecules, there are transitions between rotational and vibrational levels in addition to electronic transitions. Hence, molecular spectra are more complicated than that of atoms. It is classified according to the type of molecular energy that is being emitted or absorbed.[2]

i) Rotational Spectra : It is obtained due to the change in rotational energy of the molecule.

ii) Vibrational Spectra : It is obtained due to the change in vibrational energy of the molecule.

iii) Electronic Spectra : It is obtained due to changes in the energy of molecules due to different electronic arrangements.

The detailed information about the molecular structure (i.e. molecular symmetry, bond distance and bond angles) and chemical properties (electronic distribution, bond strength, intra and inter-molecular processes) can be obtained from the molecular spectra.

1.1.2 Important Parameters related to Molecular Structure:

While studying molecular structure, we have to study various parameters related to molecular structure such as force constant (k_e), dissociation energy (D_e), vibrational frequency (ω_e), unharmonicity ($\omega_e x_e$), etc. These parameters are determined for a number of diatomic molecules with the help of rotational and vibrational analysis.[3]

The force constant 'k_e' measures the stiffness of the bond. It gives the restoring force per unit displacement from the equilibrium position. The force constant is also equal to the curvature of the potential energy function.

'ω_e' is the vibrational frequency of anharmonic oscillator for an infinitesimal amplitude. It also gives the spacing of the energy levels (expressed in cm^{-1}) that would occur if the potential curve were a parabola with the curvature that the actual curve has at the minimum, or equilibrium position.

The coefficient '$\omega_e X_e$' is known as the anharmonicity constant. It is always much less than the principal term 'ω_e'. The anharmonicity term introduces an effect which decreases the spacing of the higher energy levels.

If a bond is stretched far enough, it will break, i.e. the molecules can be dissociated. The general shape of potential energy versus the internuclear distance is given in Fig.1.1. The height of the asymptote above the lowest vibrational level is equal to the work that must be done in order to dissociate the molecule and it is known as the dissociation energy of the molecule. The dissociation energy is given by:

$$D_e = \frac{\omega_e^2}{4\omega_e X_e}$$

The constant 'B' is the rotational constant and its value is given by:

$$B = \frac{h}{8\Pi^2 CI}$$

The rotational constant 'D' is known as the centrifugal distortion constant. The constant 'D' depends upon the vibrational frequency 'ω_e' of the molecules. For smaller ω_e, the potential curve will be flatter, hence, the influence of centrifugal force will be greater and hence, 'D' will be greater. The value of 'D' is given by $D = 4B^3/\omega^2$.

In order to investigate the spectrum on the basis of quantum theory of rotating-vibrating system, the molecule can be treated as rigid rotator, non-rigid rotator, harmonic oscillator, anharmonic oscillator or vibrating rotator and the results are summarised in Table 1.1

1.2 Various Forms for Force Constant in Diatomics:

We know that for the classical harmonic oscillator, the separation of the successive vibrational level is equal to the classical vibrational frequency, i.e. $h\nu osc$. This is true for unharmonic oscillator. The decrease of classical vibrational frequency with the increase of amplitude of vibration is same as decrease of vibrational quantum with increase in vibrational quantum number. Then according to classical theory, the exact expression for vibrational frequency of anharmonic oscillator in the state v is:

$$\nu osc(v) = C\Delta Gv$$

Here, ΔGv is used instead of $\Delta Gv+\frac{1}{2}$, so that the vibrational frequency in the state v is intermediate between the two adjacent vibrational quanta $\Delta G_{v+\frac{1}{2}}$ and $\Delta G_{v-\frac{1}{2}}$. Therefore, the vibrational quanta ΔG are sometimes referred to as the vibrational frequency. Hence, we can write:

$$\nu osc(v) = c[(\omega_e - \omega_e x_e) - 2\omega_e x_e v]$$

For the unrealizable state $v = -\frac{1}{2}$, the vibrational energy is zero and $\nu osc(-\frac{1}{2}) = c\omega_e$ Therefore, ω_e is the vibrational frequency of anharmonic oscillator for an infinitesimal amplitude. The force constant may be determined from the vibrational frequency, ω_e. We know that:

$$\nu osc = \frac{1}{2}\Pi\sqrt{k/\mu}$$

$$\therefore \quad ke = 4\Pi^2\mu c^2\omega_e^2 = 5.8883 \times 10^{-2}\mu_A\omega_e^2 \text{ dynes/cm.}$$

For infinitesimal amplitudes, cubic and higher powers of $(r-r_e)$ can be neglected in the potential energy. Hence, we can write:

$$V_{r \to r_e} = f(r-r_e)^2 = \frac{1}{2}k_e(r-r_e)^2 \quad \ldots \quad (1.3)$$

Therefore, the force constant 'k_e' determines the parabola, which is in agreement with the actual potential curve in the neighbourhood of minimum.

It is well known that the force constant 'k_e' increases with the bond order. Therefore, other things being equal, a double bond is stronger than a single bond, a triple bond is stronger than double bond. The bond order may be regarded as the measure of electronic cloud, which is responsible in holding the two atoms together.[4]

1.3 Potential Energy Functions:

For a diatomic molecule in a physically stable state, the potential energy is minimum when there is equilibrium separation between the nuclei of the two atoms. This equilibrium separation is determined by the balance between the attractive force due to electronic binding and the coulombic repulsion between the charged nuclei. If the atoms are brought closer than their equilibrium separation, then the repulsive force between two nuclei increases. Hence, the potential energy must increase due to the work done against their increasing repulsive force. If the atoms are drawn apart, then also the potential energy increases due to the work done against the superior electronic binding. As the separation between the two atoms increases, the potential energy also increases and it will reach a limiting value which is called as the dissociation energy of the molecule. This simple fact of the molecular system gives rise to potential energy curve with a minimum at equilibrium internuclear distance, sharp rise towards infinity as the nuclei are brought closer together and less sharp rise towards dissociation limit as the separation is increased.

In the study of molecular structure, it is very important to represent correctly the potential energy of a set of atoms as a function of internuclear distance. From potential energy curve, we can obtain a good deal of information about molecular structure.[5] The minima of the potential energy curve determines the bond length. The second derivative of the potential energy with respect to distance gives the force constant. The force constant determines the vibrational and rotational levels of the molecule. The higher derivatives of potential energy curves give anharmonicity constant.

The potential energy curve can be plotted by making use of energy levels themselves. Oldenberg,[6] Rydberg[7,8] and Klein[9] have developed this method. Rosenberg[10] Almy and Beiler[11] have used Klein's method for the upper electronic states of LiH and KH, respectively. But the method is very laborious. Rees[12,13] has given analytical formulation of the Klein-Rydberg method and from this, P.E. curve can be evaluated accurately in the region of minimum. The most widely used method is to represent P.E. curve by a suitable function. Following are some criteria for a good potential energy function.[14-16] These are divided into two parts, i.e. [a] necessary, and [b] desirable.

a) Necessary:

1. At $r \rightarrow \infty$, it should come asymptotically to a finite value;
2. At $r = re$, it should have minimum,
3. At $r = 0$, it should become infinite. This need not be very strict. If U is very large at $r=0$, It gives good result.

b) Desirable:

These criteria gives the conventional form of the potential energy curve as shown in Fig.1.2.

But this is not the only possible form. There are curves with one maximum between main minimum and the dissociation limit. Multiple maxima and minima are also observed[17,18] and are shown in Figs.1.3 and 1.4.

The maxima often arises when attrative potential is crossed by a repulsive potential curve. If the interaction is not too strong, it leads to a potential maximum of the lower of the resulting potential curve. Maxima also arises due to van der Waals interaction.

For such states, Frost and Musulin[18] have given a theoretical discussion of various criteria. According to them:

$$U = \frac{Z_1Z_2e^2}{r} + Ue$$

where, $\frac{Z_1Z_2e^2}{r}$ = nuclear repulsive potential corresponding coulomb potential $\frac{Z_1Z_2e^2}{r}$, Z_1Z_2 effective atomic numbers, Ue = Purely electronic energy.

Hence, the potential function should also satisfy the following conditions.

4. (i) Ue is finite at $r = 0$

(ii) At $r = 0$, $Ue = Ue^\circ$, Ue° is united atomic energy.

5. For large r, $U_e \propto \frac{Z_1 Z_2 e^2}{r}$
6. $\frac{dU_e}{dr} = 0$ at $r = 0$.
7. Van der Waals term should introduce terms of the form $1/r^n$

The criterion 4 to 7 need not be exactly true.

When the molecule is vibrating, then we can see that for any vibrational energy state, the internuclear distance varies between two fixed values.[17] This motion is similar to the simple harmonic motion. In this type of motion, we can see that the molecule will spend most of its time at the two limits of vibration. At these two limits, the molecule is most likely to undergo an electronic transition. These limits of vibration are known as the turning points and these are the points of maximum intensity. Various methods are suggested to obtain these classical turning points.[19 to 23]

1.4 F.C.Factors and r-centroids for Diatomics:

With the help of Franck-Condon Principle, the different cases of intensity distribution are explained. On the basis of quantum theory, Condon[24] has shown that in case of given electronic transition in a diatomic molecule, certain transitions were most probable than the others. His calculations were based on Frank's[25] assumption, i.e. during an electronic transition, nuclei, which are originally in a non-vibrating state, remain momentarily fixed because of their large mass, compared with those of electrons. But because of the motion of electrons, the equilibrium distance between two nuclei is altered. Hence, nuclei acquire potential energy with respect to new equilibrium distance and begins to vibrate. In this case, the amplitude of vibration is equal to the change in equilibrium separation. If the nuclei vibrating in the initial state, then almost any amplitude in the end state is possible. But these are the positions where the nuclei spend most of the time. These are the turning points of the vibratory motion. Condon had shown that these positions lie along the parabolic path in the double entry table and this agrees well with the experiment.

The idea of quantum theory may be carried over to new quantum mechanics. In new mechanics, the intensity of spectral line may be obtained by evaluating the integral of product of electric moment and the wave function of initial and final state. The probability of transition between two states characterized by ψ' and ψ'' is proportional to the square of the corresponding matrix element of the electric moment or the transition moment, i.e.

$$R = \int \psi'^{*} M \psi'' d\tau$$

where, M is a vector with components $\Sigma c_i x_i$, $\Sigma c_i y_i$ and $\Sigma c_i z_i$

Further, neglecting rotation, we can write:

$$\psi = \psi_e \psi_v$$

where, ψ_e = electronic and ψ_v = vibrational eigen function.

We can resolve M (i.e. electric moment) in two parts, one depending on nuclei and other depending on nucleus, i.e. $M = M_e + M_n$. Substituting this in equation (1.4) and after simplification, we get

$$R = \psi_v{}'\psi_v{}'' \, dr \quad \int Me \, \psi_e'^{*} \psi_e'' \, d\tau_c$$

The second integral:

$$Re = \int Me \psi_e'^{*} \psi_e'' d\tau_c$$

is the electronic transition moment. But the variation of Re with r is slow and we can replace Re by an average value $\bar{Re}$.

$$\therefore \quad R^{v'v''} = \bar{Re} \int \psi_v' \psi_v'' \, dr$$

The transition probability which is proportioned to square of R is given by:

$$P^{v'v''} = \frac{64\Pi^3}{3h^4c^3} E^3_{v'v''} \left(\int \psi_v' \, Re(r) \psi_v'' dr\right)^2$$

where, $E_{v'v''}$ = the energy quantum of the band.

The vibrational transition probability may be defined as:

$$P_{v'v''} = \left(\int \psi_v' Re(r) \psi_v'' dr\right)^2$$

Re(r) is assumed to be a smoothly varying function of r and the above equation can be written as:

$$P_{v'v''} = Re^2(r_{v'v''}) \left(\int \psi_v' \psi_v'' dr\right)^2$$

$$= R_e^2 \, (r_{v'v''}) q_{v'v''}$$

Here, $q_{v'v''} = \left(\int \psi_v' \psi_v'' dr\right)^2$

is the Franck-Condon factor of the band system. Franck-Condon factor largely controls the intensity distribution of vibrational bands. Various methods of determining F.C. factors are available in the literature.[26-33]

r-Centroids:

The dependence of $R_e(r)$ on r is generally unknown and as a first approximation, $R_e(r)$ can be replaced by a mean value $\bar{R}_e$ for the band system. But if the dependence of $R_e(r)$ on r is either known or sought, then the integrals:

$$_0\int^{\infty} \psi_1^{(v')} r \psi_2^{(v'')} dr \equiv (v',rv'') \qquad \ldots \qquad (1.5)$$

$$_0\int^{\infty} \psi_1^{(v')} r^2 \psi_2^{(v'')} dr \equiv (v',r^2v'') \qquad \ldots \qquad (1.6)$$

become of interest. Jarmain[34] and Fraser[35] noticed that these integrals exhibited the following property, i.e.

$$\frac{(v',rv'')}{(v',v'')} = \frac{(v'r^2v'')}{(v'rv'')}$$

The accuracy in almost all cases is better than 2%. Equality of this ratio could be extended to higher powers of r.

$$\therefore \quad \frac{(v',rv'')}{(v',v'')} = \frac{(v',r^nv'')}{(v'r^{n-1}v'')}$$

Here, the upper limit on the power of r is of the order of 10. A quantity $\bar{r}_{v'v''}$, which may be considered as an average r for the $(v' \longrightarrow v'')$ transition may be defined as,

$$\bar{r}_{v'v''} = \frac{(v'rv'')}{(v'v'')}$$

This quantity $\bar{r}_{v'v''}$ is called the **r-centroid** of the band system. It is the characteristic internuclear separation, i.e. the average of all internuclear distances and is given by:

$$\bar{r}_{v'v''} = \frac{\int \psi_{v'} r \psi_{v''} dr}{\int \psi_{v'} \psi_{v''}\, dr}$$

The concept of r-centroid was first introduced by Nicholls and Jarmain.[36] They have suggested different methods for the evaluation of r-centroids. The graphical method suggested by them is easier and can be applied to all diatomic molecules.

1.5 Our approach towards getting correct values of these parameters.

In this Dissertation, we have reported theoretical research investigations on the various parameters related to diatomic molecular structure. The potential energy function, F.C. factors, r-centroids are obtained by applying quantum mechanical principles to the spectra emitted by diatomic molecules. We have undertaken the critical studies on various methods of finding out these parameters for certain diatomic molecules. The results are reported in three different Chapters.

In Chapter-II, we have carried out a work on force constants and some parameters such as anharmonicity constant, zero point mean square amplitude, electronegativity that depend on force constant. Force constants are obtained by using different relations as suggested by Cordy, Badger for diatomic halides, deuteroids and other molecules. New expressions for force constants have been suggested and the force constants are computed by employing these proposed relations. The values of force constants are compared with the experimental data. It is observed that our expressions yielded in giving better values of force constant than those of Gordy and Badger. Similarly, anharmonicity constant $\omega_e X_e$ and zero point mean square amplitude $\langle (r-re) \rangle$ are computed by employing our proposed relations for force constant. The results are tabulated along with experimental values and we found that the constants $\omega_e X_e$ and $\langle (r-re) \rangle$ obtained by using our relations are in better agreement with the experimental values. Further, in the same Chapter, we have calculated band order using the concept of covalence force for a number of diatomic molecules. These values of bond order are used to obtain force constants and zero point mean square amplitudes by using proposed relations.

In Chapter-III, we have carried out a work on potential energy functions. An outline of basic theory leading to the formation of potential energy curve is given and the importance of these curves in the determination of potential energy curve is explained. Rapid method to construct potential energy curve from RKRV data is discussed at length and this method is applied for the determination of classical turning points of electronic states of different diatomics. We also have proposed new functional formulae for diatomic molecular potential. Using these expressions, we have obtained classical turning points for B and X states 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 states of SiTe, X state of LuF and $A^3\Pi_0$, $B^3\Pi_1$ and $X'\Sigma^+$ states of InBr. The classical turning points are determined employing Lakshman and Rao method for the B and X states of XeF and $A^2\Delta_{5/2}$, $B^2\Delta_{5/2}$, $X^2\Delta_{5/2}$ states of PtH and PtD. The results are then compared with those obtained by following RKRV procedure.

In Chapter-IV, we have reported our results on Franck-Condon Factors and r-centroids in the case of certain diatomics. The Franck-Condon factors are determined using Bates Method, Manneback Method and Fraser-Jarmain Method for the band systems $A'\Pi$-$X'\Sigma$ and $B'\Sigma$-$X'\Sigma^+$ of CuF, $E^2\Delta_{5/2}$-$X^2\Pi_{1/2}$ of CuO, $A^2\Sigma$-$X^2\Pi_i$ of CuSe, A-X of CuTe, $A^2\Pi$-$X^2\Sigma$ of AlSe, $d'\Sigma^+$-$C'\Pi^+$ and $d'\Sigma^+$-$b'\Sigma^+$ of NH, $d'\Sigma^+$-$c'\Pi$ of ND and $A'\Pi$-$X'\Sigma^+$ of PN, $A^3\Pi_0$-$X'\Sigma^+$ and $B^3\Pi_1$-$X'\Sigma^+$ of InBr molecules.

The r-centroids are determined by Nicholls-Jarmain technique for band systems $A'\Sigma$-$X'\Sigma^+$ of CuF, $A^2\Sigma+$-$X^2\Pi_i$ of CuSe, A-X of CuTe, $A^2\Pi$-$X^2\Sigma$ of AlSe, B-X of XeF, $A^3\Pi_0$-$X'\Sigma^+$ and $B^3\Pi_1$-$X'\Sigma^+$ of InBr. The r-centroids are also computed by using functional relation for B-X system of XeF, $A^3\Pi_0$-$X'\Sigma^+$ and $B^3\Pi_1$-$X'\Sigma^+$ system of InBr. It is found that the proposed functional relation of potential energy function yielded in giving beter data on r-centroids.

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TABLE 1.1

Summary of the Results considering Diatomic Molecules according to Different Models.

Model	Term Value	Wave Number	Nature of Spectrum
Rigid Rotator	$F(J) = BJ\,(J+1)$	$2B\,(J+1)$	Spectrum consists of series of equidistant lines.
Harmonic Oscillator	$G(U) = (\nu osc/c) \times (U + \frac{1}{2})$	$\nu = \omega$	The frequency of radiated light is equal to the frequency (νosc) of the oscillator. All of the allowed transitions give rise to the same frequency.
Anharmonic Oscillator	$G(v) = \omega\,(v+\frac{1}{2}) - \omega\,x\,(v+\frac{1}{2})^2 +$	$\nu osc = \omega_0 v' - \omega_0 x_0 v'^2\ \omega_0 y_0 v'^3 + \ldots$	Energy levels are not equidistant like harmonic -oscillator, but their separation decreases slowly with increasing v. The observed absorption frequencies give directly the position of vibrational levels above the lowest vibrational level.
Non-rigid Rotator	$F(J) = BJ(J+1) - DJ^2(J+1)^2$	$\nu = 2B(J+1) - 4D(J+1)^2$	The lines are no longer exactly equidistant, as for the rigid rotator, but their separation decreases slightly with increasing J.
Vibrating Rotator	$T = G(v) + F_v(J)$ $= \omega_e(v+\frac{1}{2}) - \omega_e x_e (v+\frac{1}{2})^2$ $+ \ldots + B_v J(J+1)$ $- D_v J^2(J+1)^2 + \ldots$	$\nu = \nu_0 + B_v' J'(J'+1) - B_v'' J''(J''+1)$ $\nu_R = \nu + 2B_v' + (3B_v' - B_v'')J + (B_v' - B_v'')J^2,$ $J = 0, 1, \ldots.$ $\nu_p = -(B_v' - B_v'')J + + (B_v' - B_v'')J^2,$ $J = 0, 1, 2, \ldots$	Two series of equidistant lines are observed. One going from towards shorter wavelength side and other ν going towards longer wavelength side. There is no transition of ν_0 i.e. zero gap.

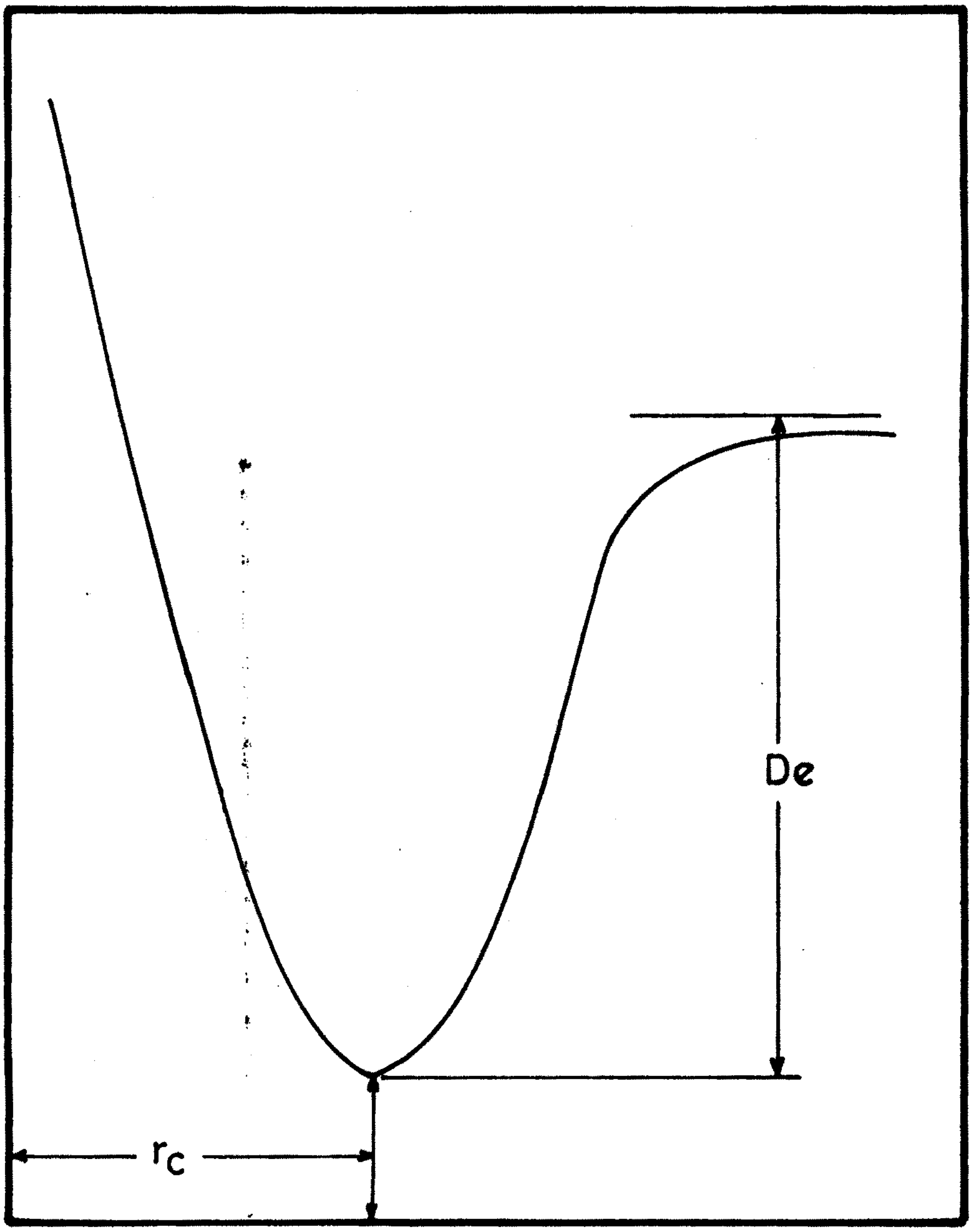

Fig.1·1 – THE GENERAL SHAPE OF POTENTIAL ENERGY CURVE.

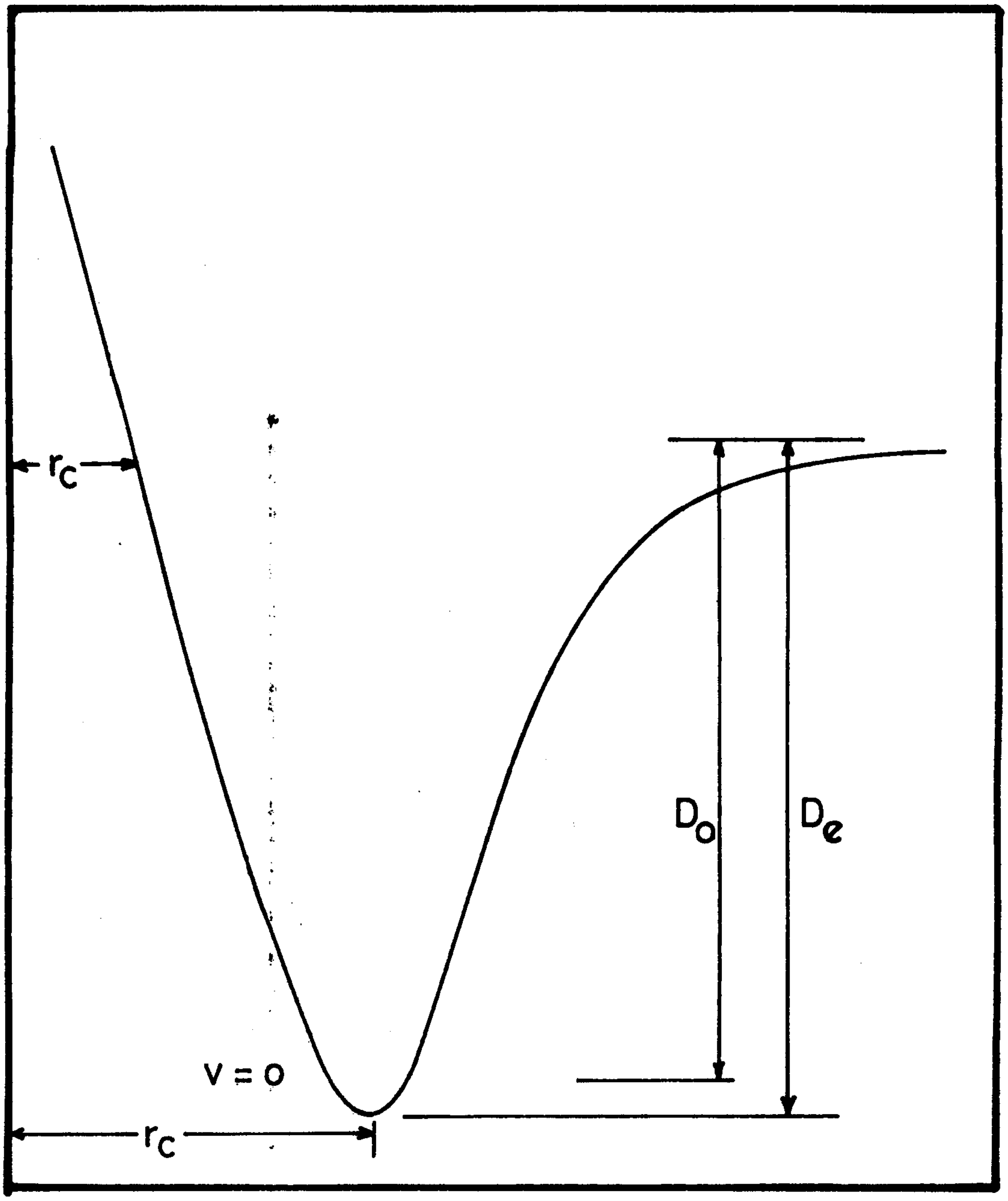

Fig. 1·2 – THE CONVENTIONAL FORM OF THE POTENTIAL ENERGY CURVE.

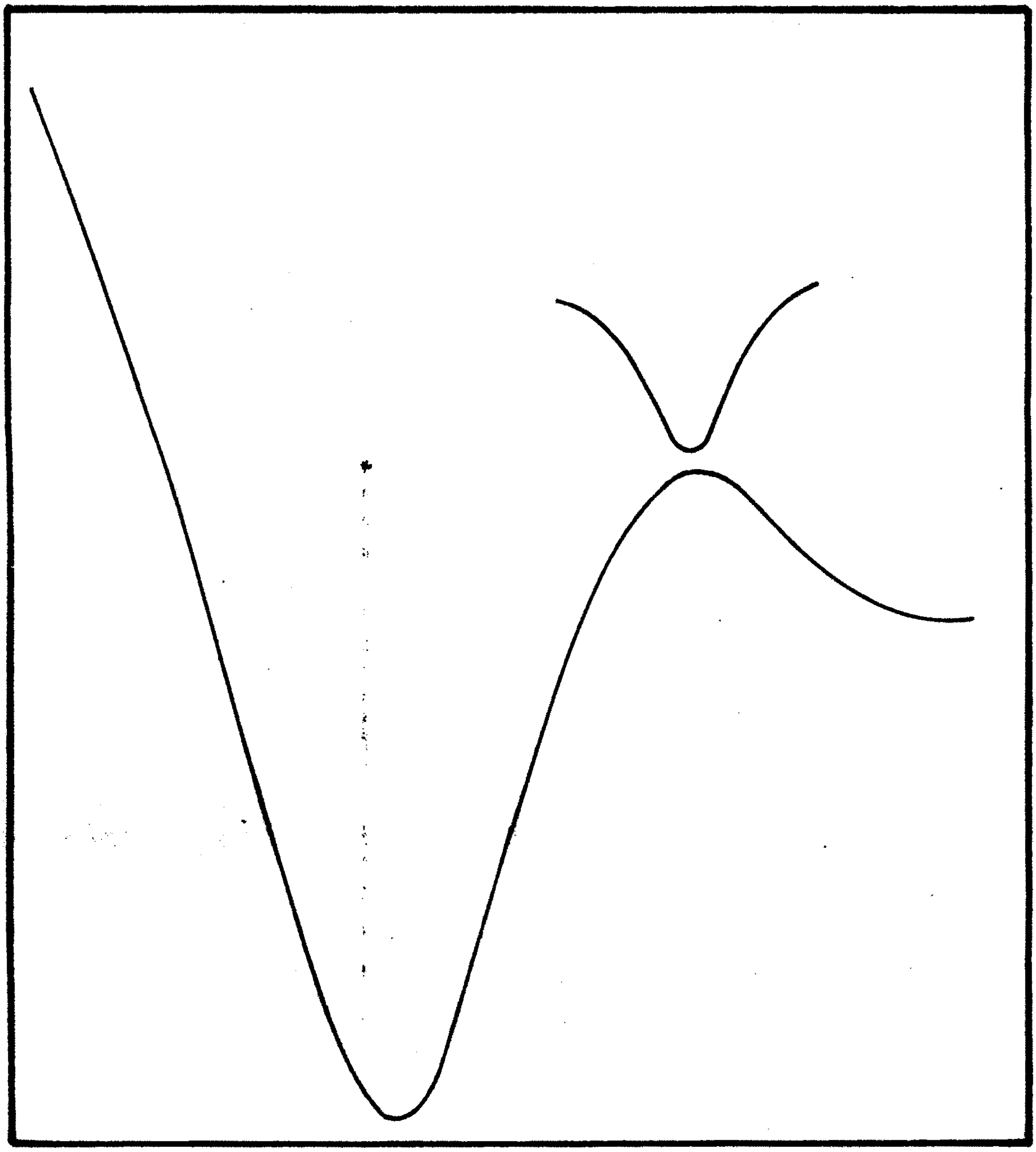

Fig. 1·3 - Potential curve with one maximum lying above dissociation limit.

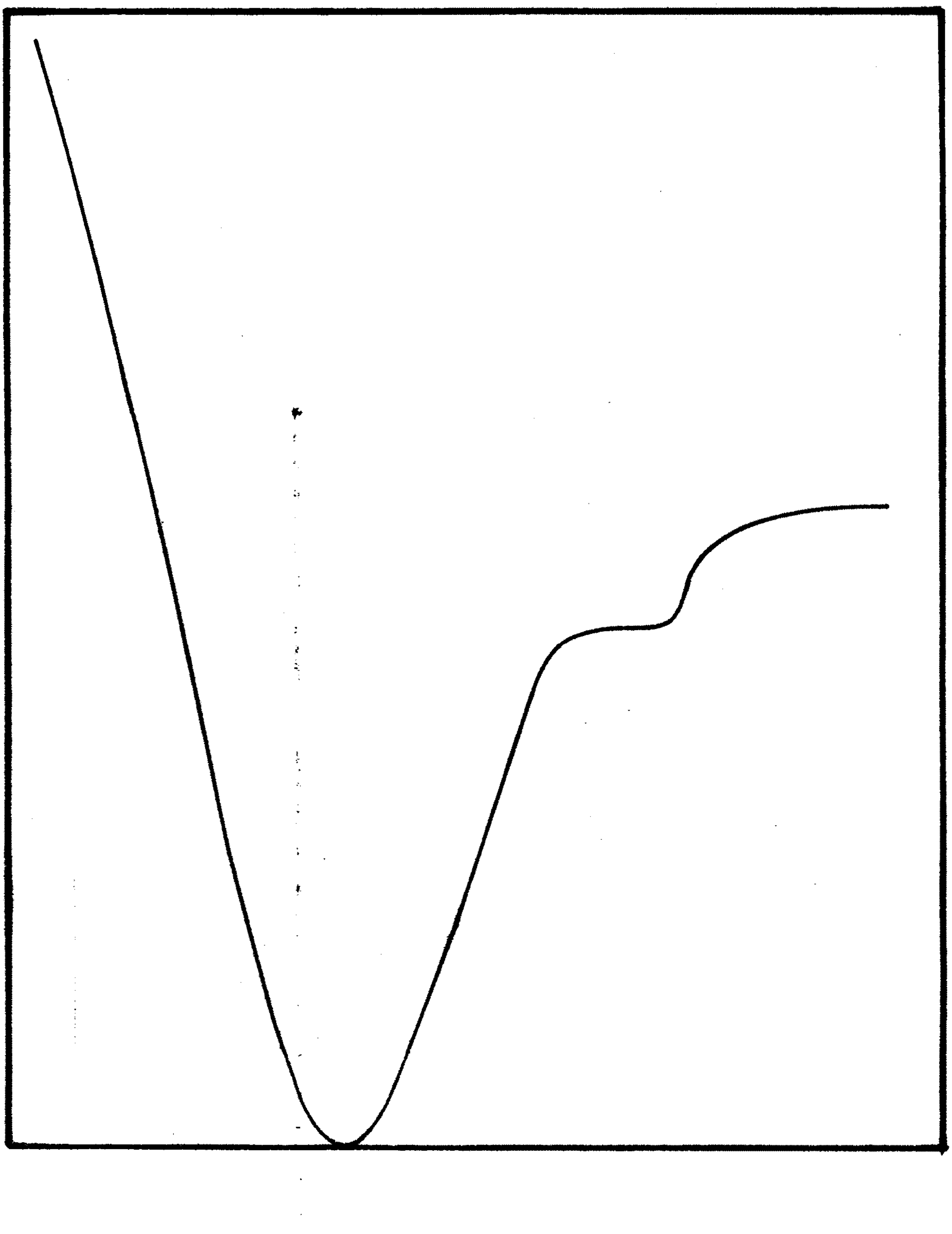

Fig. 1·4 – Maximum lies below dissociation limit.