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DISSOCIATION ENERGY OF GROUND STATE OF GaCl MOLECULE

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The dissociation energy of a diatomic molecule is an important constant. There are various methods to determine this constant. One of these methods is potential energy curves using correlation coefficient, which is employed in the present paper to calculate the dissociation energy of diatomic Gallium chloride using the Hulber- Hirschfelderpotential function.

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1. Introduction

The importance of diatomic molecular spectroscopy is well-known in the Physical sciences, Chemical physics, Thermodynamics, Molecular physics and Astrophysics. In general, studies in the above branches need spectroscopic information like molecular constants, dissociation energies, bond lengths etc. [1-3].In the present work the Dissociation energy of GaCl is estimated using the latest constants and the correlation coefficient method.

Group IIIA halides are of great interest to molecular spectroscopists as few of them show the potential laser transitions [4,5]. Under optimal experimental conditions,GaCl, GaBr, InBretcmolecules show strong emission bands in the visible region. There are some bound free transitions in these molecules and the situation is therefore favorable for lasing action. In addition, a few band systems like $A^3\Pi_0$ - X $^1\sum^+$ and B^3 Π_1 - X $^1\sum^+$ show intense bands. Many workers [6,7] and the references therein have studied the band spectra of GaCl in emission as well as in absorption. The emission band spectra of GaCl, especially in UV region, consist of two overlapping violet degraded band systems, namely $A^3\Pi_0$ - X $^1\sum^+$ and B^3 Π_1 - X $^1\sum^{+.}$ The spectra of GaCl in the 28,000 to 30,000 cm^{-1}region was obtained using a Fourier Transform Spectrometer BOMEM DA 8 with an apodized resolution of 0.035 cm-^{1} [8].The molecular constants derived by them are used in the present work and are reported in Table 1.

2. Methods of calculation

2.1 Dissociation energy of diatomic molecules

The height of an asymptote of a potential energy curve, above the lowest vibrational level, is equal to the work that must be done in order to dissociate that molecule,and is known as the heat of dissociation or dissociation energy D^0. Another constant D_e is also the dissociation energy but it is taken as a height of an asymptote from x-axis or measured from minima of the potential energy curve. The relation between $D^0$and D_e is

$$\text{here } D_e=D^0+G(0) \tag{1}$$

$$\text{where } G(0) = \omega_e/2 - \omega_e x_e/4 + \omega_e y_e/8+\ldots.. \tag{2}$$

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Since no distinguishable vibrational level lies above the asymptote, D_e is also defined as the maximum value of G(v)

$$D_e = \Delta G_{max}(v) \tag{3}$$

Another relation in defining the dissociation energy De in terms of molecular constants is

$$D_e = \omega_e^2/4\omega_e x_e$$

There are various ways to determine the D^0namely 1) Band convergence limit 2) Extrapolation to convergence limit, 3) Long wavelength limit of an absorption continuum, 4) Predissociationlimit, 5) Excitation of atomic fluorescence, 6) photodissociation 7) chemiluminescence etc.

The extrapolation to convergence limit is also known as Birge and Sponer's linear extrapolation method.[1] This method is frequently employed to determine the dissociation energy from experimentally observed vibrational quanta ΔG, which is plotted against v. The area under the curve gives the $D^{0.}$ Experimentally observed vibrational levels are few in number and since cubic and quartic and higher order terms in the potential function are neglected, the curve drawn between ΔG versus v appears like a straight line. Detailed discussion of D^0 can be found in texts [1-3] as well as a specific monograph by Gaydon [9]. This method gives D_e 20% higher than the actual value.

2.2 Potential energy curves

As discussed earlier, potential energy functions could be employed to calculate the dissociation energy. Dissociation energy can be estimated by comparing the potential energies at different r values from the RKR curves and using a particular potential function. For example, the potential energy at r using RKR curves is, for example, $U_{RKR}(r)$. At the same r value, the potential function under study may give the value $U_{poten} = D_e.F(r)$. The F(r) part can be evaluated at that r .The fitting or matching of U_{RKR} and U_{Poten} demands that

$$U_{RKR}(r) = D_e\, F(r) \quad (4)$$

As mentioned before many popular potential functions are employed for this purpose.

2.2.1 The H – H potential function

This function is defined as follows.

$$U_{H\text{–}H}(r) = D_e\{[1- \exp\{-a(r- r_e)\}]^2 + cx^3(1+ bx)\exp(- 2x)\} \tag{5}$$

where D_e is dissociation energy

$$a = \omega_e/[2(B_e D_e)^{1/2} r_e] \tag{6}$$

$$c = 1+ a_1(D_e/a_0)^2 \tag{7}$$

$$b = 2 - \{[(7/12) - (D_e.\, a_2)/a_0] / c\} \tag{8}$$

$$a_0 = \omega_e^2/4B_e \tag{9}$$

$$a_1 = -1 - [\omega_e \alpha_e/6B_e^2] \tag{10}$$

$$a_2 = [5/4]a_1^2 - [2/3][\omega_e x_e/ B_e] \tag{11}$$

All constants have their usual meanings. a_0, a_1 and a_2 are known as Dunham coefficients.

2.3 The method of correlation coefficients

Rao et al [10-12] have suggested a statistical method to calculate D_e using calculations ofcorrelation coefficients. This method is applied to calculate the dissociation energies of HgCl, HgBr and HgI [13], CrF [14], ScO, YO, and LaO [15] molecules by different workers.

The potentials often match to RKR curves in the vicinity of r_e, i.e., at low quantum numbers or in the harmonic part of an oscillator. But at higher v , i.e. for anharmonic parts, the U values of the potential curves don't tally to RKR and the curves can fit along Y coordinate passing through r = r_e . Systematic deviations still show the best fits, but only if the average of U values for $r_{min}$and r_{max} are taken. In order to overcome such difficulties the correlation coefficient parameter is used. The correlation coefficient 'r' between two variables Xiand Y_i is defined as

$$r = \frac{N\Sigma X_i Y_i - \Sigma X_i \Sigma Y_i}{[N\Sigma X_i^2 - (\Sigma X_i)^2]^{1/2} \, . \, [N\Sigma Y_i^2 - (\Sigma Y_i)^2]^{1/2}} \qquad (12)$$

where N is total number of observations, i.e. i = 1 to N . It is clear that

ΣX_i^2 differs from $(\Sigma X_i)^2$and$\Sigma X_i Y_i$ differs from $\Sigma X_i \Sigma Y_i$

The two sets X_i and Y_i correlate with each other maximum when r→1. Now suppose a potential function under study is U = D_e F(r). One can assign a certain value to $D_{e,}$ say 1ev and by substituting various r_{min} and r_{max} values obtained from RKRV curves one can evaluate U values. These U values and U values calculated using RKR form the two sets i.e. X_i and $Y_{i..}$ Thus.a correlation coefficient can be calculated for D_e = 1ev. Now change the values of De and repeat the same procedure and obtain a new correlation coefficient. Normally the dissociation energies of diatomic molecules range from 1ev to 10 ev. The D_e for maximum values of correlation coefficient should be selected, say it is 5 ev then in the next trial range of the D_e 's from 4.5 to 5.5,ev is chosen varying by 0.1 ev. If suppose the maximum correlation coefficient appears to 5.3 ev than repeat the procedure for getting 0.001 ev accuracy and thus the D_e value giving maximum correlation can be obtained.

The dissociation energy for various diatomic molecules are calculated using H-H function, Lippincott function& electronegativity potential function. In many cases the H-H function gives best correlation as the coefficient approaches to 1. However the correlation is poor in the case of Lippincott and electronegativity potential functions. In the case of the other potential functions, the correlation coefficient can also be calculated, but it is quite cumbersome.

3. Results and discussion

In the present study, the Hulbert Hirschfelder potential is used to determine dissociation energy using correlation coefficient method. Using the most recent vibrational and rotational constants, which are based on experimental studies, the RKRV curves are constructed. The H-H function is used to calculate dissociation energy for this molecule. The correlation coefficient method gives D_e = 4.5eV for GaCl molecule. This value is in good agreement with the value 4.9eV, and also in agreement with Huber and Hertzberg. The correlation coefficients are given in Table 2 and the comparative P.E.curves are shown in Fig 2.

Table 1. Molecular constants of GaCl

Molecular Constants	**GaCl**
μ	23.199015
ω_e	365.668
$\omega_e x_e$	5.910
B_e	0.149913
α_e	0.0007936
D_e	39865
r_e	2.20178

All quantities are in cm^{-1} except r_e which is in A^0

Table 2 : Correlation between Hulbert-Hirschfelder function and RKR potential energy curves of GaCl molecule.

D_e (eV)	**Correlation Coefficient**
1	0.546369
2	0.778833
3	0.951897
4	0.99609
4.3	0.998693
4.4	0.999016
4.45	0.999095
4.46	0.999105
4.47	0.999113
4.48	0.999119
4.49	0.999123
4.5	**0.999126**
4.51	0.999126
4.52	0.999124
4.53	0.999121
4.54	0.999116
4.6	0.999051
4.7	0.998817
4.8	0.998445
4.9	0.997956
5	0.997365
5.1	0.996689
6	0.988403
7	0.977979
8	0.968259

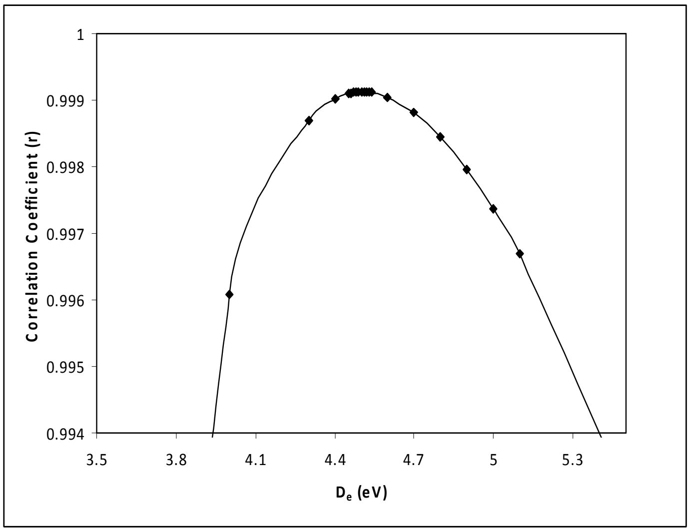

Fig.1: Graph of Correlation Coefficient Vs D_e for the ground state ofGaCl molecule

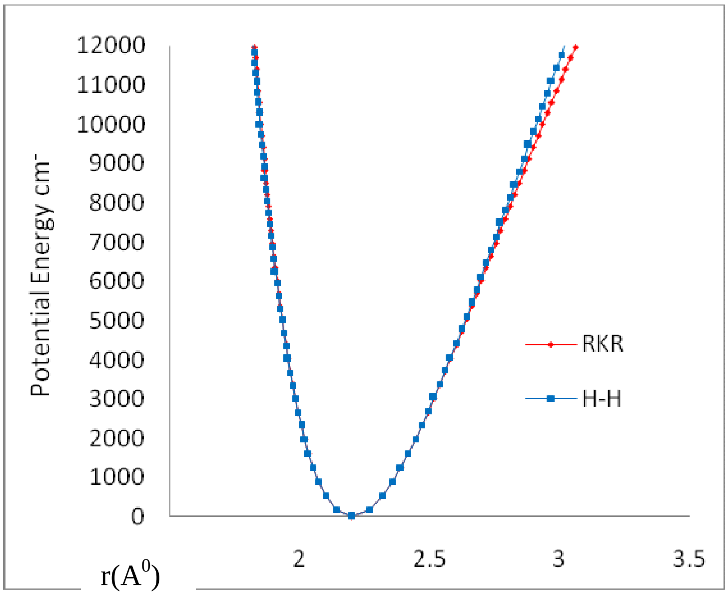

Fig. 2: RKR and H-H Potential energy curves for the ground state of GaCl

4. Conclusions

The conclusion is that the dissociation energy calculated using H-H potential function and the method of correlation coefficients is in good agreement with experimental values

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