

Dissociation Energy of Ground State of GaCl Molecule

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ABSTRACT

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The dissociation energy of a diatomic molecule is an important constant. There are various methods to determine this constant. A method of potential energy curves using correlation coefficient is one of them. This method is employed in present paper to calculate the dissociation energy of diatomic Gallium chloride using the Hulber- Hirschfelder potential function.

I. INTRODUCTION

The importance of diatomic molecular spectroscopy is well-known in Physical sciences, Chemical physics, Thermodynamics, Molecular physics and Astrophysics. In general, the studies in 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 method of correlation coefficients.

Group IIIA halides are of great interest to the molecular spectroscopists as few of them show the potential laser transitions [4,5]. Under optimal experimental conditions GaCl, GaBr, InBr etc molecules shows strong emission bands in visible region. There are some bound free transitions in these molecules and therefore the situation is favorable for lasing action. Besides these few band systems like $A^3\Pi_0 - X^1\Sigma^+$ and $B^3\Pi_1 - X^1\Sigma^+$ 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 consisting of two overlapping violet degraded band systems namely $A^3\Pi_0 - X^1\Sigma^+$ and $B^3\Pi_1 - X^1\Sigma^+$. The spectra of GaCl in the region 28,000 to 30,000 cm^{-1} 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.

II. 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, which is called 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

Where

$$D_e = D^0 + G(0) \quad \dots\dots\dots(1)$$

$$\text{Where } G(0) = \omega_e/2 - \omega_e x_e/4 + \omega_e y_e/8 + \dots\dots \quad \dots\dots (2)$$

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

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

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

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

There are various ways to determine the D^0 , namely

- 1) Band convergence limit
- 2) Extrapolation to convergence limit,
- 3) Long wavelength limit of an absorption continuum,
- 4) Predissociation limit,
- 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 curve gives the D^0 many a times 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. The detailed discussion on D^0 could be found in texts [1-3] and a specific monograph by Gaydon [9]. This method gives D_e 20% higher than the actual value.

III. DISSOCIATION ENERGY FROM THE POTENTIAL ENERGY CURVES

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

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

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

IV. THE H – H POTENTIAL FUNCTION

This function is defined as follows.

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

where D_e is dissociation energy

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

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

$$b = 2 - \{ [(7/12) - (D_e \cdot a_2)/a_0] / c \} \quad \text{-----}(8)$$

$$a_0 = \omega_e^2 / 4B_e \quad \text{-----}(9)$$

$$a_1 = -1 - [\omega_e \alpha_e / 6B_e^2] \quad \text{-----}(10)$$

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

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

V. THE METHOD OF CORRELATION COEFFICIENTS

Rao et al [10-12] have suggested a statistical method to calculate D_e using calculations of correlation 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.

Many a times the potentials 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 $r = r_e$. The systematic deviations still show best fits, 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 X_i and Y_i is defined as

$$r = \frac{N \sum X_i Y_i - \sum X_i \sum Y_i}{\sqrt{[N \sum X_i^2 - (\sum X_i)^2] \cdot [N \sum Y_i^2 - (\sum Y_i)^2]}} \quad (12)$$

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

$\sum X_i^2$ differs from $(\sum X_i)^2$ and $\sum X_i Y_i$ differs from $\sum X_i \sum Y_i$. The two sets X_i and Y_i correlate with each other maximum when $r \rightarrow 1$. Now suppose a potential function under study is $U = D_e F(r)$. One can assign certain value to D_e , say 1 eV and by substituting various r_{\min} and r_{\max} values obtained from RKR curves one can evaluate U values. These U values and U values calculated using RKR from the two sets i.e X_i and Y_i . Thus, a correlation coefficient can be calculated for $D_e = 1$ eV. Now change the values of D_e and repeat the same procedure and get correlation coefficient. Normally the dissociation energies of diatomic molecules range from 1 eV 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 then 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 case of Lippincott and electronegativity potential functions. In case of the other potential functions the correlation coefficient can be calculated but it is quite cumbersome.

VI. DISCUSSION AND CONCLUSIONS

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 RKR curves are constructed. The H-H function is used to calculate dissociation energy for this molecule. The correlation coefficient method gives $D_e = 4.5$ eV for GaCl molecule. This value is in good agreement with the value 4.9 eV, and also in the agreement Huber and Hertzberg. The correlation coefficients are given in table 2 and the comparative P.E. curves are shown in fig 2.

Finally the conclusion is that the dissociation energy calculated using H-H potential function and the method of correlation coefficients gives good agreement to experimental value.

Table 1. Molecular constants of GaCl

Molecular Constants	GaCl
μ	23.199015
ω_e	365.668
ω_{exe}	5.910
B_e	0.149913
α_e	0.0007936
D_e	39865
r_e	2.20178

All the constants are in cm^{-1} except r_e which is in \AA and μ which is in amu

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

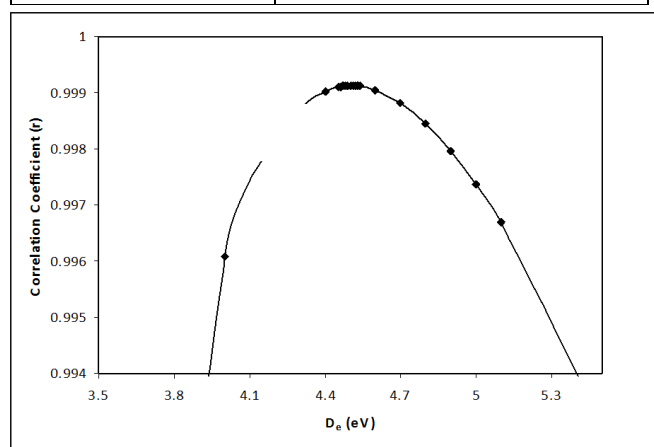


Figure1. Graph of Correlation Coefficient Vs D_e for the ground state of GaCl molecule

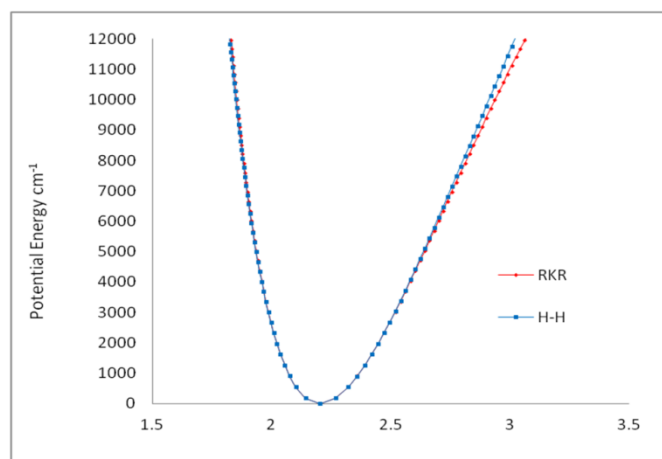


Fig. 2 RKR and H-H Potential energy curves for the ground state of GaClr (A0)

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