

DISSOCIATION ENERGY OF THE CaBr MOLECULE

R. R. REDDY¹⁾, A. S. R. REDDY¹⁾, Suddarah, T. V. R. RAO²⁾, Anantapur

The experimental potential energy curves for the $X^2\Sigma^+$ and the $V^2\Sigma^+$ states of CaBr have been constructed using the method of Lakshman and Rao. The ground state dissociation energy of the molecule has been estimated as 2.230 ± 0.069 eV by the curve fitting procedure.

ЭНЕРГИЯ ДИССОЦИАЦИИ ДЛЯ МОЛЕКУЛЫ CaBr

В статье на основе метода Лакшмана и Рао построены экспериментальные кривые потенциальной энергии для состояний $X^2\Sigma^+$ и $V^2\Sigma^+$ молекулы CaBr. Энергия диссоциации основного состояния молекулы, которая имеет значение $2,230 \pm 0,069$ эВ, определена при помощи метода подходящей аппроксимации кривой.

1. INTRODUCTION

The knowledge of the precise value of the dissociation energy of diatomic molecules is of fundamental importance for thermochemistry and it is often of interest in astrophysics. The present paper deals with the construction of potential energy curves for the $X^2\Sigma^+$ and the $V^2\Sigma^+$ states of the CaBr molecule using the method of Lakshman and Rao [1] and the estimation of dissociation energy for the ground state of the molecule by fitting the three-parameter Lippincott potential function [2] with the constructed potential energy curve. The molecular constants in the equilibrium position, viz. the electronic term (T_e), the vibrational constants ($w_e, w_e X_e$), the rotational constants (B_e, α_e) and the internuclear distance (r_e) of the molecule, required for the present work have been taken from the work of Bernath et al. [3] and are given in Table 1. Many investigators [4, 5] have studied the other halides of calcium. Since so far there has been no report about the construction of potential energy curves and the theoretical estimation of the dissociation energy of the CaBr molecule, the present authors have taken up this investigation.

¹⁾ Department of Physics, KSRM College of Engineering, CUDDAPAH 516 001, India.

²⁾ Department of Physics, S. K. University, ANANTAPUR 515 003, India.

Table 1

Molecular constants for $X^2\Sigma^+$ and $B^2\Sigma^+$ states of CaBr

State	T_e [cm ⁻¹]	w_e [cm ⁻¹]	$w_e x_e$ [cm ⁻¹]	B_e [cm ⁻¹]	α_e [cm ⁻¹]	r_e [nm]
$X^2\Sigma^+$	0	285.732	0.840	0.094466141	0.000403551	0.259377
$B^2\Sigma^+$	16383.137	285.747	0.954	0.096515100	0.000448300	0.256609

II. POTENTIAL ENERGY CURVE

The method of Lakshman and Rao [1] is an improved form of the RKR method and was successfully verified for several states belonging to different diatomic molecules in a number of cases [1, 6—10]. Chakraborty and Pan [11] mentioned in their review paper that the method of Lakshman and Rao is reliable and accurate.

The maximum (r_{max}) and minimum (r_{min}) values of the internuclear distance for a molecule vibrating with energy U_i are given in terms of f and g as

$$r_{max} = \left[\frac{f}{g} + f^2 \right]^{1/2} + f$$

and

$$r_{min} = \left[\frac{f}{g} + f^2 \right]^{1/2} - f$$

where

$$f = \left[\frac{8\pi^2 \mu c (wx)}{h} \right]^{-1/2} \ln W_i$$

and

$$g = \left(\frac{2\pi^2 \mu c}{h} \right)^{1/2} \{ 2\alpha_i (wx)_i^{-1} U_i^{1/2} + (wx)_i^{-1/2} \times \\ + [2B_i - \alpha_i w_i (wx)_i^{-1}] \ln W_i \}$$

in which

$$W_i = \frac{[w_i^2 r_i - 4(wx)_i U_i]^{1/2}}{[w_i - 2(wx)_i^{1/2} U_i^{1/2}]}$$

and

$$U_i = w_i(v+1/2) - (wx)_i(v+1/2)^2.$$

In the above relations, μ is the reduced mass of the molecule, c is the velocity of

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Table 2

Turning points of the potential energy curves of CaBr

v	U_i [cm ⁻¹]	$X^2\Sigma^+$ State		r_e [nm]	r_{max} [nm]
		$U_i + T_e$ [cm ⁻¹]	r_e [nm]		
0	142.656	142.656	0.25289	0.259377	0.26624
1	426.708	426.708	0.24852	0.259377	0.27170
2	709.080	709.080	0.24565	0.259377	0.27566
3	989.772	989.772	0.24341	0.259377	0.27900
4	1268.784	1268.784	0.24153	0.259377	0.28199
5	1546.116	1546.116	0.23989	0.259377	0.28473
		$B^2\Sigma^+$ State			
0	142.635	16525.772	0.25014	0.256609	0.26349
1	426.474	16809.611	0.24579	0.256609	0.26899
2	708.405	17091.542	0.24295	0.256609	0.27298
3	988.428	17371.565	0.24073	0.256609	0.27636
4	1266.543	17649.680	0.23887	0.256609	0.27939
5	1542.750	17925.887	0.23726	0.256609	0.28218

light and h is the Planck constant and the notations are the same as adopted by Vanderslice et al. [12].

Four consecutive vibrational terms are taken at a time and using the least square method the constants w_i and $w_i x_i$ are determined. They are used only over the middle two levels. Similarly from the next set of four overlapping levels constants for other successive levels are determined. The rotational constants B_e and α_e are taken as B_i and α_i , respectively as the variation in their values is negligible with the vibrational quantum number (v) for any electronic state.

III. DISSOCIATION ENERGY

An accurate evaluation of dissociation energy from curve fitting requires a good empirical potential function. The three-parameter Lippincott potential function [2] has been shown to reproduce well RKR curves over a wide range of energies and for a number of diatomic molecules [13—19]. The Lippincott function as modified by Steele [2] is

$$U(r) = D_e \left[1 - \exp \left\{ \frac{-n(r-r_e)^2}{2r} \right\} \right] \left[1 - a \left(\frac{b^2 A}{2r} \right)^{1/2} (r-r_e) \right] \times \\ \times \exp \left\{ - \left(\frac{b^2 A}{2r} \right)^{1/2} (r-r_e) \right\}$$

Table 3

Estimation of dissociation energy of the CaBr molecule
Comparison of the observed and the calculated energy values

r [nm]	U [cm^{-1}]	$D_e = 2.21 \text{ eV}$ $U(r)$ [cm^{-1}]	$D_e = 2.23 \text{ eV}$ $U(r)$ [cm^{-1}]	$D_e = 2.25 \text{ eV}$ $U(r)$ [cm^{-1}]
0.26624	142.656	138.057	139.610	141.162
0.27170	426.708	416.886	421.575	426.263
0.27566	709.080	694.718	792.531	710.344
0.27900	989.772	971.149	982.071	992.993
0.28199	1268.784	1246.067	1260.081	1274.095
0.28473	1546.116	1519.416	1536.504	1553.592
0.28522	142.656	144.475	146.100	147.725
0.24852	426.708	427.764	432.575	437.385
0.24565	709.080	708.209	716.173	724.138
0.24341	989.772	986.199	997.290	1008.381
0.24153	1268.784	1261.831	1276.002	1290.213
0.23989	1546.116	1535.144	1552.409	1569.674
Average % deviation		1.351	1.073	1.224

in which

$$a = \frac{F}{1 + \frac{5}{4}F}, \quad n = \frac{2F^2}{r_c(ab)^2}, \quad \text{where } b = 1.065 \text{ and } F = \frac{\alpha W}{6B_2^2}.$$

The Lakshman and Rao turning points are used in the above expression and for a particular value of D_e , the energy values $U(r)$ are compared with U_i . The procedure has been repeated for different values of D_e . The value (2.23 eV) for which the best fit obtains is taken to be the dissociation energy of the molecule.

IV. RESULTS AND DISCUSSION

The turning points obtained for twelve vibrational levels of the two electronic states of the CaBr molecule are presented in Table 2.

The most characteristic feature of these curves is that they are narrow-well type potentials which indicate that the molecule behaves approximately like a harmonic oscillator. The true potential energy curves lie approximately one above the other indicating the structure of the molecule in the ground state and the upper states to be nearly the same. This is evident from approximately equal r_e values for these states.

It is obvious from Table 3 that the best fitting of the energy values is achieved for $D_e = 2.23 \text{ eV}$ since the average percentage deviation in this case is minimum

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(1.073). Thus, $D_e = 2.230 \pm 0.069 \text{ eV}$; the error indicated in the D_e value takes into account the error of 3% inherent to the Lippincott potential function and the error involved in the curve fitting.

However, this estimated value is lower than the value (3.28 eV) recommended by Huber and Herzberg [20]. Gaydon's [21] suggested value is 4.08 eV. The ground state of the molecule. In the present case, the $H-H$ function predicts a higher value. The above statement may be explained by the opinion of Steele et al. [22] i.e., no single potential function is suitable to represent the energy values, nor can we choose a function which gives the best fit of the energy values.

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