

## Short Communication

### Dissociation energy of the BiF molecule

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#### Abstract

The experimental potential energy curves for  $X^3\Sigma^-$ ,  $A^3\Sigma^-$  and  $C^1\Pi$  states of the BiF molecule have been constructed by the method of Lakshman and Rao. The ground state dissociation energy of the molecule has been estimated as  $3.33 \pm 0.40$  eV by the curve fitting procedure.

**Key words :** Potential energy (RKR) curves, dissociation energy, Lippincott potential function.

#### 1. Introduction

A 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  $X^3\Sigma^-$ ,  $A^3\Sigma^-$  and  $C^1\Pi$  states of BiF molecule using the method of Lakshman and Rao<sup>1</sup> and the estimation of dissociation energy for the ground state of the molecule by fitting the three-parameter Lippincott potential function<sup>2</sup> with the constructed potential energy curve. The molecular constants in the equilibrium position, viz., the electronic term ( $T_e$ ), the vibrational constants ( $\omega_e, \omega_e x_e$ ) the rotational constants ( $B_e, \alpha_e$ ) and the internuclear distance ( $r_e$ ) of the molecule, required for the present work have been taken from Mizushima<sup>3</sup> and are given in Table I.

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Table I

## Molecular constants of BiF molecule

Constant	$X^3\Sigma^-$	$A^3\Sigma^-$	$C^1\Pi$
$T_0$ (cm <sup>-1</sup> )	0	22959.70	44222.00
$\omega_0$ (cm <sup>-1</sup> )	510.00	381.00	615.00
$\omega_0 x_0$ (cm <sup>-1</sup> )	2.05	3.00	2.50
$B_0$ (cm <sup>-1</sup> )	0.2301	0.2101	0.2500
$a_0$ (cm <sup>-1</sup> )	0.0012	0.0007	0.00132
$r_0$ (Å)	2.05	2.15	1.97

## 2. Potential energy curves

With the Rydberg-Klein-Rees (RKR) method<sup>4</sup> one can construct very accurate potential energy curves close to the minimum only, from the experimentally measured molecular constants of a diatomic molecule. The method of Lakshman and Rao<sup>1</sup> is an improved form of RKR method and was successfully verified for several states belonging to different diatomic molecules in a number of cases<sup>5-10</sup>. Chakraborty and Pan<sup>11</sup> had 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

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

where

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

and

$$g = \left( \frac{2\pi^2 \mu c}{h} \right)^{1/2} \{ 2a_i (\omega x)_i^{-1} U_i^{1/2} + (\omega x)_i^{-1/2} [2B_i - a_i \omega_i (\omega x)_i^{-1}] \ln W_i \}$$

in which

$$W_i = \frac{[\omega^2 - 4(\omega x)_i U_i]^{1/2}}{\omega_i - 2(\omega x)_i^{1/2} U_i^{1/2}}$$

and

$$U_i = \omega_i \left( v + \frac{1}{2} \right) - \omega_i x_i \left( v + \frac{1}{2} \right)^2.$$

In the above relations,  $\mu$  is the reduced mass of the molecule,  $c$  is the velocity of light and  $h$  is the Planck's constant and the notations are the same as adopted by Vanderslice *et al*<sup>12</sup>.

Four consecutive vibrational terms are taken at a time, and using the least square method, the constants  $\omega_i$  and  $(\omega x)_i$  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  $B_v$  and  $a_v$  are taken as  $B_i$  and  $a_i$  respectively as the variation in their values is negligible with the vibrational quantum number ( $v$ ) for any one electronic state.

### 3. Dissociation energy

In evaluating the dissociation energy of a molecule by the method of curve fitting, the three parameter Lippincott potential function has been shown to reproduce quite well the RKR curves wherever these are known over a wide range of energy, for a number of diatomic molecules<sup>13-15</sup>.

The Lippincott potential function used is of the form,

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

in which

$$a = \frac{F}{1 + \frac{5}{4}F}, \quad n = \frac{2F^2}{r_e(ab)^2}$$

where  $b = 1.065$  and  $F = a_e \omega_e / 6B_e^2$ .

The turning points of the ground state of BiF, obtained in the present study, are used in the Lippincott function and for a particular value of  $D_e$ , the observed energy values of  $U_i$  are compared with the calculated energy values  $[U(r)]$ . This procedure is repeated for different values of  $D_e$  and the  $D_e$  value (27100 cm<sup>-1</sup>), for which the best fit of the energy values is observed, is taken as the precise dissociation energy of the molecule. For comparison purpose the calculated energy values for different  $D_e$  values are presented in Table III.

### 4. Results and discussion

The turning points obtained for forty-five vibrational levels of the three electronic states of BiF molecule are presented in Table II.

Table II

Turning points of the potential energy curves of BiF

$v$	$U_v$ (cm <sup>-1</sup> )	$U_v + T_0$ (cm <sup>-1</sup> )	$r_{\min}$ (Å)	$r_{\max}$ (Å)
<u>X<sup>3</sup>Σ<sup>-</sup> State</u>				
0	254.48	254.48	1.9879	2.1112
1	760.37	760.37	1.9478	2.1622
2	1262.19	1262.19	1.9217	2.1994
3	1759.88	1759.88	1.9011	2.2309
4	2253.48	2253.48	1.8840	2.2592
5	2742.98	2742.98	1.8691	2.2854
6	3228.38	3228.38	1.8558	2.3099
7	3709.68	3709.68	1.8438	2.3333
8	4186.88	4186.88	1.8328	2.3558
9	4659.98	4659.98	1.8226	2.3775
10	5128.98	5128.98	1.8132	2.3986
11	5593.88	5593.88	1.8043	2.4192
12	6054.68	6054.68	1.7959	2.4394
13	6511.38	6511.38	1.7880	2.4592
14	6963.98	6963.98	1.7805	2.4787
15	7412.48	7412.48	1.7734	2.4979
16	7856.88	7856.88	1.7665	2.5170
17	8297.18	8297.18	1.7600	2.5358
18	8733.38	8733.38	1.7537	2.5544
19	9165.48	9165.48	1.7477	2.5729
<u>A<sup>3</sup>Σ<sup>-</sup> State</u>				
0	189.76	23149.46	2.0766	2.2195
1	565.09	23524.79	2.0283	2.2773
2	935.31	23895.01	1.9960	2.3194
3	1301.04	24260.74	1.9701	2.3551
4	1662.86	24622.56	1.9488	2.3862
5	2021.39	24981.09	1.9297	2.4152
6	2377.21	25336.91	1.9125	2.4425
7	2730.94	25690.64	1.8966	2.4685
8	3083.16	26042.86	1.8838	2.4911
9	3434.49	26394.19	1.8707	2.5139
10	3785.51	26745.21	1.8585	2.5363
11	4136.84	27096.53	1.8469	2.5581
12	4489.06	27448.76	1.8390	2.5749
13	4842.79	27802.49	1.8294	2.5942
14	5198.61	28158.31	1.8202	2.6133
<u>C<sup>1</sup>Π State</u>				
0	306.88	44528.88	1.9133	2.0256
1	916.88	45138.88	1.8769	2.0722
2	1521.88	45743.88	1.8532	2.1062
3	2121.88	46343.88	1.8347	2.1350
4	2716.88	46938.88	1.8192	2.1609
5	3306.88	47528.88	1.8057	2.1849
6	3891.88	48113.88	1.7938	2.2074
7	4471.88	48693.88	1.7829	2.2288
8	5046.88	49268.88	1.7731	2.2495
9	5616.88	49838.88	1.7639	2.2694

Table III

Estimation of dissociation energy of BiF molecule—comparison of the observed and calculated energy values

$r$ (Å)	$U_i$ cm <sup>-1</sup>	$D_0 = 27400$ cm <sup>-1</sup>		$D_0 = 27100$ cm <sup>-1</sup>		$D_0 = 26800$ cm <sup>-1</sup>	
		$U(r)$ cm <sup>-1</sup>	% deviation	$U(r)$ cm <sup>-1</sup>	% deviation	$U(r)$ cm <sup>-1</sup>	% deviation
1.9879	254.49	281.61	10.65	278.53	9.45	275.44	8.23
2.1112	254.49	229.38	9.87	226.87	10.85	224.36	11.84
1.9011	1759.88	1839.29	4.51	1819.15	3.36	1799.01	2.22
2.2309	1759.88	1702.46	3.26	1683.82	4.32	1665.18	5.38
1.8558	3228.38	3345.74	3.64	3309.11	2.50	3272.48	1.37
2.3099	3228.38	3167.77	1.88	3133.08	2.95	3098.40	4.03
1.8226	4659.98	4818.41	3.40	4765.66	2.27	4712.90	1.14
2.3775	4659.98	4611.91	1.03	4561.41	2.12	4510.92	3.20
1.7959	6054.68	6257.69	3.35	6189.18	2.22	6120.66	1.09
2.4394	6054.68	6029.69	0.41	5963.67	1.50	5897.65	2.59
1.7734	7412.48	7663.42	3.39	7579.51	2.25	7495.61	1.12
2.4979	7412.48	7415.46	0.04	7334.27	1.06	7253.08	2.15
1.7537	8733.38	9049.63	3.62	8950.54	2.49	8851.46	1.35
2.5544	8733.38	8768.53	0.40	8672.53	0.07	8576.52	1.80
		Average	3.53	Average	3.38	Average	3.40

It is obvious from Table III that the best fitting of the energy values is achieved for  $D_0 = 3.36$  eV since the average percentage deviation in this case is minimum. Hence the dissociation energy for the ground state of BiF is  $3.36 \pm 0.40$  eV and the value as measured from the lowest vibrational level is  $D_0 = 3.33$  eV. But the estimated value is slightly higher than the value ( $2.65 \pm 0.3$  eV) recommended by Gaydon<sup>16</sup>.

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#### References

1. LAKSHMAN, S. V. J. AND RAMAKRISHNA RAO, T. V. *J. Phy. B*, 1971, 4, 269.

2. STEELE, D. AND LIPPINCOTT, E. R. *J. Chem. Phys.*, 1961, 35, 2065.
3. MIZUSHIMA, M. *Rotating diatomic molecules*, John Wiley Sons, New York, 1975.
4. REES, A. G. L. *Proc. Phys. Soc.*, 1947, 59, 998.
5. LAKSHMAN, S. V. J., RAMAKRISHNA RAO, T. V. AND TIMMA NAIDU, G. *Pramāna*, 1976, 7, 369.
6. LAKSHMAN, S. V. J., RAMAKRISHNA RAO, T. V. AND TIMMA NAIDU, G. *Curr. Sci.*, 1977, 46, 33.
7. RAMAKRISHNA RAO, T. V. AND RAMAKRISHNA REDDY, R. *Physica*, 1978, 95C, 412.
8. RAMAKRISHNA RAO, T. V., NAIDU, G. T. AND RAMAKRISHNA REDDY, R. *Indian J. Pure Appl. Phys.*, 1979, 17, 842.
9. RAM SAMUJH RAM, RAI, S. B. AND UPADHYA, K. N. *Indian J. Pure Appl. Phys.*, 1979, 17, 844.
10. RAMAKRISHNA RAO, T. V. AND RAMAKRISHNA REDDY, R. *Acta Physica Hungarica*, 1980, 48, 25.
11. CHAKRABORTY, B. AND PAN, Y. K. *Appl. Spectrosc. Rev.*, 1973, 7, 283.
12. VANDERSLICE, J. T., MASON, E. A., MAISCH, W. G. AND LIPPINCOTT, E. R. *J. Molec. Spectrosc.*, 1959, 3, 17 ; 1960, 5, 83.
13. ASTHANA, B. P., KUSHAWAHA, V. S. AND NAIR, K. P. R. *Acta Physica Polonica*, 1972, A42, 739.
14. NAIR, K. P. R., RAM B. SINGH AND RAI, D. K. *J. Chem. Phys.*, 1965, 43, 3570.
15. RAMAKRISHNA RAO, T. V. AND LAKSHMAN, S. V. J. *Curr. Sci.*, 1971, 40, 316.
16. GAYDON, A. G. *Dissociation energies and spectra of diatomic molecules*, Chapman and Hall Ltd., London, 1968.