

THE RKR CURVES AND DISSOCIATION ENERGY OF AlF MOLECULE

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ABSTRACT

The true potential energy curves for $X^1\Sigma^+$, $A^1\Pi$, $C^1\Sigma^+$, $D^1\Delta$, $E^1\Pi$, $F^1\Pi$, $b^3\Sigma^+$, $c^3\Sigma^+$ states of AlF molecule have been calculated by Lakshman and Rao's (present authors) method as well as Rydberg Klein-Rees as modified by Vanderslice *et al.* method, the agreement between the two is excellent. Dissociation energy and Ionization Potential for this molecule have been estimated as 7.016 eV and 9.696 eV respectively, which are in good agreement with the values given by Barrow *et al.*

INTRODUCTION

THE band spectrum of AlF has been investigated in emission by many investigators¹⁻⁵ and recently by Barrow *et al.*⁶ and in all, twelve band systems for AlF molecule have been observed and analysed. The rotational and vibrational constants required in the present work are presented in Table I.

mine the vibrational and rotational energy levels of the molecule. The positions of these vibrational and rotational energy levels determine the thermodynamic properties of the substances. Gas imperfections are due to potential energy changes in molecular collisions while reaction rates are determined by the potential energy surface of the activated complex of the reacting molecule.

TABLE I

Molecular constants of AlF molecule

State	T_e cm ⁻¹	ω_e cm ⁻¹	$\omega_e x_e$ cm ⁻¹	$\omega_e y_e$ cm ⁻¹	B_e cm ⁻¹	$\alpha_e \times 10^3$ cm ⁻¹	r_e Å
$X^1\Sigma^+$	0	802.26	4.77	..	0.55250	4.95	1.6542
$A^1\Pi$	43949.2	803.94	5.99	-0.050	0.55640	5.34	1.6484
$C^1\Sigma^+$	57688.0	938.22	5.09	-0.017	0.58992	4.58	1.6009
$D^1\Delta$	61229.5	901.05	6.11	..	0.58297	5.02	1.6104
$E^1\Pi$	63689.4	923.02	5.28	..	0.58709	4.64	1.6047
$F^1\Pi$	65795.6	955.33	5.38	..	0.59281	4.59	1.5970
$b^3\Sigma^+$	44813.2	786.37	7.64	-0.009	0.56280	6.51	1.6390
$c^3\Sigma^+$	54957.7	933.66	4.81	..	0.58861	4.57	1.6026

The molecules N₂, CO, BF, SiO, SiS, CS and AlF have rather similar spectra. In continuation of the work on SiO and SiS molecules, the authors took up the present work on AlF molecule.

The construction of potential energy curves is of considerable importance for the understanding of kinetic mechanisms, spectral phenomena, stellar structure and many associated problems⁷⁻⁹. Potential energy minima determine the possible structures and are thus related to bond strength and valence. The curvatures of the potential energy surface, the second derivatives of the potential energy with respect to the distance in certain specified directions are the force constants for various modes of vibration and deter-

THE TRUE POTENTIAL ENERGY CURVES

The present paper deals with the construction of potential energy curves for different electronic states $X^1\Sigma^+$, $A^1\Pi$, $C^1\Sigma^+$, $D^1\Delta$, $E^1\Pi$, $F^1\Pi$, $b^3\Sigma^+$, $c^3\Sigma^+$ of AlF molecule using the Rydberg-Klein-Rees method as modified by Vanderslice *et al.*¹⁰⁻¹¹ along with the Lakshman and Rao's method¹². The RKR method has been considered to be superior to the Morse method, since it can be used upto the dissociation limit, unlike Morse method whose validity lies in regions near the potential minimum. Even though the vibrational levels are few in number in the different states of AlF molecule, the RKR method is preferred to the Morse method, since the α_e as calculated from Pekeris relation (Herzberg)¹³ deviates ranging from 1 to 11% in different electronic states to the experi-

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mentally observed α_e values in the different electronic states. This method which is known as RKR method is a WKB approximation from which we obtain reliable potential energy curves from the measured vibrational and rotational analyses of the diatomic molecules.

The present method by Lakshman and Rao¹² was successfully verified by them in number of cases¹⁴⁻¹⁶ and recently Chakraborty and Pan¹⁷ in their review paper gave a detailed account of different methods and the authors' method is one such reliable and accurate, which involves less complicated mathematical calculations. Since the details of this method are reported in literature¹², only the explicit formulae to evaluate the classical turning points are given below:

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

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

where

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

the symbols have their usual spectroscopic significance. The classical turning points are given by the relation

$$r_{\max, \min} = \left(\frac{f}{g} + f^2 \right)^{1/2} \pm f.$$

RESULTS AND DISCUSSION

Employing the authors' method the potential energy curves for the different electronic states of AlF molecule have been calculated and the results are presented in the Table II. The agreement between the RKR

TABLE II

The true potential energy curves for different electronic states of AlF molecule

V	RKR method			Authors' method	
	$U + T_e$ (cm ⁻¹)	r_{\max} (Å)	r_{\min} (Å)	r_{\max} (Å)	r_{\min} (Å)
	1	2	3	4	5
	$T_e = 0$				
	$X^1 \Sigma^+$ state				
0	399.9	1.719	1.596	1.719	1.596
1	1192.7	1.772	1.558	1.772	1.558
2	1975.8	1.811	1.533	1.811	1.533
3	2749.5	1.845	1.514	1.845	1.514
4	3514.2	1.875	1.498	1.876	1.499

TABLE II (Contd.)

	1	2	3	4	5
	$T_e = 43949.2 \text{ cm}^{-1}$				
	$A^1 \Pi$ state				
0	44349.7	1.713	1.590	1.713	1.590
1	45141.5	1.767	1.552	1.767	1.552
2	45920.8	1.807	1.528	1.807	1.527
3	46687.5	1.841	1.509	1.842	1.510
4	47441.2	1.873	1.494	1.873	1.493
5	48181.5	1.903	1.480	1.903	1.480
6	48908.2	1.931	1.468	1.930	1.468
7	49620.7	1.958	1.457	1.958	1.457
	$T_e = 57688.0 \text{ cm}^{-1}$				
	$C^1 \Sigma^+$ state				
0	58155.8	1.660	1.547	1.660	1.547
1	59083.8	1.709	1.511	1.709	1.511
2	60001.4	1.745	1.488	1.745	1.488
3	60908.6	1.775	1.470	1.775	1.470
4	61805.3	1.806	1.453	1.806	1.453
5	62692.4	1.828	1.442	1.828	1.442
	$T_e = 61229.5 \text{ cm}^{-1}$				
	$D^1 \Delta$ state				
0	61678.5	1.672	1.555	1.672	1.555
1	62567.4	1.721	1.519	1.722	1.520
2	63444.0	1.758	1.496	1.758	1.497
	$T_e = 63689.4 \text{ cm}^{-1}$				
	$E^1 \Pi$ state				
0	64149.6	1.665	1.550	1.665	1.551
1	65062.1	1.714	1.514	1.715	1.515
2	65964.0	1.750	1.491	1.750	1.490
	$T_e = 65795.6 \text{ cm}^{-1}$				
	$F^1 \Pi$ state				
0	66271.9	1.656	1.543	1.656	1.543
1	67216.5	1.704	1.508	1.704	1.508
2	68150.3	1.739	1.485	1.739	1.485
	$T_e = 44813.2 \text{ cm}^{-1}$				
	$b^3 \Sigma^+$ state				
0	45204.5	1.705	1.581	1.705	1.581
1	45975.5	1.760	1.543	1.760	1.544
2	46731.3	1.802	1.519	1.802	1.520
3	47471.6	1.839	1.501	1.840	1.500
4	48196.4	1.872	1.486	1.872	1.486
5	48905.7	1.904	1.473	1.904	1.473
6	49599.3	1.934	1.461	1.934	1.460
7	50277.4	1.961	1.450	1.960	1.450
	$T_e = 54957.7 \text{ cm}^{-1}$				
	$c^3 \Sigma^+$ state				
0	55423.4	1.662	1.548	1.662	1.548
1	56347.4	1.711	1.512	1.711	1.512
2	57261.8	1.746	1.489	1.746	1.490
3	58166.6	1.777	1.471	1.778	1.470

method and authors' new method is excellent. It is therefore concluded that this new method can also be employed in the construction of potential energy curves in the absence of computational aids as it involves less complicated mathematical calculations.

The true potential energy curves (RKR) for a molecular electronic states have been used to estimate the dissociation energies of diatomic molecules in a number of cases by fitting an empirical potential energy curve to the true potential energy curve (Steele *et al.*¹⁸⁻¹⁹; Singh, R. B. *et al.*²⁰⁻²¹, Sing, J. *et al.*²²; Nair *et al.*²³). The Hulburt-Hirschfelder function has been shown to fit to a good extent the RKR curves wherever these are known over a wide range of energy for a number of diatomic molecules (Steele *et al.*⁹)

Hulburt-Hirschfelder function

$$V = D_e [(1 - e^{-ax})^2 + ca^3 x^3 e^{-2ax} (1 + abx)]$$

where

$$x = r - r_e$$

$$a = (K_e/2D_e)^{1/2}$$

$$b = 2 - 1/c \left[7/12 - \frac{1}{a^2 r_e^2} \left(\frac{5}{4} + \frac{5F}{2} + \frac{5F^2}{4} - G/12 \right) \right]$$

$$c = 1 - \left(\frac{1}{ar_e} \right) (1 + F)$$

$$F = \frac{\alpha_e \omega_e}{6B_e^2} \text{ and } G = \frac{8\omega_e x_e}{B_e}$$

being five parameter function gives the best average results and in general gives the best or near the best fit of the potential for all the cases studied.

In the present work using Hulburt-Hirschfelder function the ground state $X^1\Sigma^+$ dissociation energy of AlF molecule is estimated as $56,587.5 \text{ cm}^{-1}$ (7.016 eV which is in very good agreement with the value ($6.85 \pm 0.1 \text{ eV}$) suggested by Gaydon²⁴. Using D_e , the ionization potential for AlF, is calculated assuming I of Al and D_e of AlF^+ from Gaydon²⁴.

$$\begin{aligned} I(\text{AlF}) &= I(\text{Al}) + D_e(\text{AlF}) - D_e(\text{AlF}^+) \\ &= 48,232.9 + 56,587.5 - 26,616.8 \\ &\approx 78,203.6 \text{ cm}^{-1} \end{aligned}$$

which is in good agreement with the value $80,000 \text{ cm}^{-1}$ (9.918 eV) given by Barrow *et al.*⁶.

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