

## TRUE POTENTIAL ENERGY CURVES AND DISSOCIATION ENERGY OF THE PS MOLECULE

S. V. J. LAKSHMAN AND M. VENKATARAMAIAH

Spectroscopic Laboratories, Department of Physics, S.V. University, Tirupati, India

## ABSTRACT

The true experimental potential energy curves of different electronic states of the PS molecule have been constructed by the method of Lakshman and Rao. The ground state Dissociation Energy of the PS molecule has been computed using the H-H function. The value is found to be in good agreement with the value reported by Gaydon.

## INTRODUCTION

THE construction of accurate Potential Energy Curves is of considerable importance for the understanding of the physical problems arising in astrophysics, gas kinetics and molecular spectra. Two band systems of the PS molecule have been reported by Dressler and Meischer<sup>1</sup> and Dressler<sup>2</sup>. The rotational analysis of the C<sup>2</sup>Σ-X<sup>2</sup>π<sub>r</sub> system of the molecule has been carried out by Balasubramanian, Dixit and Narasimham<sup>3</sup>. The vibrational and rotational constants required for the present work have been taken from Balasubramanian, Dixit and Narasimham and Huber<sup>4</sup> and are given in Table I.

Since only the B<sub>0</sub> and r<sub>0</sub> values are available for the ground X<sup>2</sup>π<sub>r</sub> state, the value of a<sub>e</sub> has been calculated using the Pekeris relation,

$$a_e = \frac{6\sqrt{x_e\omega_e B_e^3}}{\omega_e} - \frac{6B_e^2}{\omega_e}.$$

Substituting B<sub>0</sub> + a<sub>e</sub>/2 for B<sub>e</sub> in this expression. We obtain a biquadratic equation in a<sub>e</sub> namely

$$\begin{aligned} \frac{a_e^4}{16} + \left( \frac{B_0}{2} - \frac{x_e\omega_e}{8} + \frac{\omega_e}{12} \right) a_e^3 \\ + \left( \frac{3B_0^2}{2} - \frac{3B_0x_e\omega_e}{4} + \frac{\omega_e B_0}{3} + \frac{\omega_e^2}{36} \right) a_e^2 \\ + \left( 2B_0^3 - \frac{3B_0^2 x_e \omega_e}{2} + \frac{\omega_e B_0^2}{3} \right) a_e \\ + (B_0^4 - B_0^3 x_e \omega_e) = 0. \end{aligned}$$

Using Newton's method of approximation and the known value of B<sub>0</sub>, the value of a<sub>e</sub> is determined. Using this value of a<sub>e</sub> and the expression B<sub>e</sub> = B<sub>0</sub> + a<sub>e</sub>(v + ½) the value of B<sub>e</sub> is determined. The values of a<sub>e</sub> and B<sub>e</sub> thus determined are 0.001546 and 0.2962773 respectively. From the value of B<sub>e</sub>, r<sub>e</sub> is estimated to be 1.8991 Å.

## RESULTS AND DISCUSSION

The true potential energy curves have been drawn for the X<sup>2</sup>π<sub>r</sub> and C<sup>2</sup>Σ states of the PS molecule by

TABLE I  
Vibrational and rotational constants of the X<sup>2</sup>π<sub>r</sub> and C<sup>2</sup>Σ states of the PS molecule

	X <sup>2</sup> π <sub>r</sub>	C <sup>2</sup> Σ
ω <sub>e</sub>	= 739.1 cm <sup>-1</sup>	T <sub>e</sub> = 34688.7 cm <sup>-1</sup>
x <sub>e</sub> ω <sub>e</sub>	= 2.96 cm <sup>-1</sup>	ω <sub>e</sub> = 534.1 cm <sup>-1</sup>
B <sub>0</sub>	= 0.2965 cm <sup>-1</sup>	x <sub>e</sub> ω <sub>e</sub> = 3.07 cm <sup>-1</sup>
r <sub>0</sub>	= 1.9000 Å	B <sub>e</sub> = 0.2664 cm <sup>-1</sup>
		a <sub>e</sub> = 0.00195 cm <sup>-1</sup>
		r <sub>e</sub> = 2.013 Å

the method of Lakshman and Rao<sup>5</sup> for which the rotational constants are available. The turning points are given in terms of f and g as

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

and

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

where

$$f = \left( \frac{h}{8\pi^2 \mu c x_e \omega_e} \right)^{1/2} \ln W_e$$

and

$$\begin{aligned} g = \left( \frac{2\pi^2 \mu c}{h} \right)^{1/2} \frac{1}{(x_e \omega_e)^{1/2}} [ & a_e (4x_e \omega_e U)^{1/2} \\ + (2x_e \omega_e B_e - a_e \omega_e) \ln W_e ] \end{aligned}$$

$$W_e = \frac{(\omega_e^2 - 4x_e \omega_e U)^{1/2}}{\omega_e - (4x_e \omega_e U)^{1/2}}$$

The other symbols have their usual significance. The turning points obtained for X<sup>2</sup>π<sub>r</sub> and C<sup>2</sup>Σ states of the PS molecule are presented in Table II.

TABLE II

The true potential energy curves for the  $X^2\pi_g$  and  $C^2\Sigma$  states of the PS molecule

	$U \text{ (cm}^{-1}\text{)}$	$r_{\max} (\text{\AA})$	$r_{\min} (\text{\AA})$
$X^2\pi_g$ State			
0	368.81	1.9554	1.8475
1	1101.91	2.0000	1.8125
2	1829.71	2.0324	1.7895
3	2551.81	2.0600	1.7717
4	3267.71	2.0847	1.7567
5	3977.31	2.1076	1.7435
6	4680.11	2.1291	1.7319
7	5377.41	2.1496	1.7213
8	6069.61	2.1691	1.7118
$C^2\Sigma$ State			
0	266.28	2.0806	1.9536
1	794.18	2.1347	1.9136
2	1315.8	2.1746	1.8878
3	1829.5	2.2087	1.8679
4	2338.4	2.2397	1.8513

## DISSOCIATION ENERGY

The potential energy curves for different molecular electronic states can theoretically be computed by using the Hulbert-Hirschfelder<sup>6</sup> function

$$U = D [(1 - e^{-x})^2 + Cx^3 e^{-2x} (1 + bx)]$$

w. e. c

$$x = \frac{\omega_e}{2(B_e D_e)^{1/2}} \frac{r - r_e}{r_e}$$

$$c = 1 + a, (D_e/a_0)^{1/2};$$

$$b = 2 - [(7/12) - D_e a_2/a_0]/c$$

and  $a_0$ ,  $a_1$  and  $a_2$  are the constants given by

$$a_0 = \frac{\omega_e^2}{4B_e}; \quad a_1 = -1 - \frac{a_e \omega_e}{6B_e^2}$$

$$a_2 = \frac{5}{4} a_1^2 - \frac{2x_e \omega_e}{3B_e} \quad \text{and} \quad D_e = \frac{\omega_e^2}{4x_e \omega_e}.$$

This function being a five parameter function gives the best average results and in general gives the best fit of the potential. The turning points of the  $X^2\pi_g$  ground state obtained in the present work are used in the above expression and the potential energy with different values of  $D$  are calculated and are presented in Table III.

TABLE III

Calculation of Dissociation Energy of the Ground state of PS molecule using H-H function

$r \text{ \AA}$	45,000 cm <sup>-1</sup>	45,500 cm <sup>-1</sup>	46,000 cm <sup>-1</sup>	46,500 cm <sup>-1</sup>	47,000 cm <sup>-1</sup>	$U \text{ (cm}^{-1}\text{)}$
1.9554	359.5	363.5	367.5	371.5	375.5	368.8
1.8475	359.9	363.9	367.9	371.9	375.9	1101.9
2.0000	1075.0	1087.0	1097.0	1110.9	1122.8	
2.0324	1074.0	1085.9	1097.8	1109.8	1121.7	1829.7
2.0600	1782.1	1801.9	1821.7	1841.5	1861.3	
2.0847	1786.9	1806.7	1826.6	1846.4	1866.3	2551.8
2.0847	2485.7	2513.3	2540.9	2568.5	2596.1	
2.0847	2486.8	2514.4	2542.0	2569.7	2597.3	3267.7
2.0847	3181.6	3216.9	3252.3	3287.6	3323.0	
2.0847	3185.2	3220.6	3256.0	3291.4	3326.8	3977.3
2.1076	3874.0	3917.1	3960.2	4003.2	4046.3	4680.1
2.1076	3887.6	3930.8	3974.0	4017.2	4060.4	
2.1291	4559.4	4601.1	4660.7	4711.4	4762.1	5377.4
2.1291	4576.0	4627.4	4678.3	4729.1	4780.0	
2.1496	5236.4	5294.6	5352.8	540.9	5469.1	
2.1496	5260.8	5319.3	5377.7	5436.2	5494.6	6069.6
2.1691	5907.8	5973.1	6038.8	6104.4	6170.1	
2.1691	5939.1	6005.1	6071.1	6137.1	6203.1	

TABLE IV

Divergence of the Dissociation energy in eV of various molecules by different methods

Molecule	Curve fitting method	Thermochemical method	Mass spectrometric method	Other method	Gaydon
BeO <sup>9</sup>	5.15 ± 0.15 (Lippincott)	5.5	4.6 ± 0.1		4.6 ± 0.2
MgO <sup>10</sup>	3.35 ± 0.4 (Lippincott)	4.68	3.73		4.1 ± 0.6
NF <sup>11</sup>	4.48 (H-H)			3.6 ± 0.4-0.2	4.0 ± 1.0
PF <sup>11</sup>	4.98 (H-H)			4.65 ± 0.2	4.5 ± 1.0
PbF <sup>12</sup>	2.4 ± 0.2			3.22 or 3.57	3.0 ± 0.5
PS	5.7 (H-H)		4.54		5.2 ± 1.0
(Present work)					

By a comparison of the potential energy curves, the value of  $46,000 \text{ cm}^{-1}$  for D is found to give a good fit to the theoretical values. The Dissociation Energy of the molecule may therefore be  $46,000 \text{ cm}^{-1}$  or 5.7 eV. This value is in very good agreement with the value of  $5.2 \pm 1 \text{ eV}$  reported by Gaydon<sup>7</sup>.

The values of Dissociation Energies for various molecules determined by different methods show a considerable divergence as shown in Table IV. Steele *et al.*<sup>8</sup> pointed out that no single function is best fit for all molecular states considered, nor can we predict a suitable function which will give an ideal potential for a restricted range of  $r$ .

Until such time the Dissociation Energy for this molecule is determined by a different method it is difficult to say which value is the correct value.

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