

Dissociation energy of P_2^+ molecule

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Abstract. The true potential energy curves have been constructed for the different electronic states of P_2^+ molecule by the method of Lakshman and Rao. The dissociation energy for the ground state of the P_2^+ molecule has been estimated to be 4.03 eV by the method of curve fitting using the three-parameter Lippincott potential function. The ionisation potential of P_2 molecule has been estimated as 11.98 eV which is in good agreement with the value given by Gaydon.

Keywords. Dissociation energy; ionisation potential; Lippincott potential function; RKR curves.

1. Introduction

The emission spectrum of the P_2^+ molecular ion has been analysed by Narasimham (1957). The previously known $C^2\pi - X^2\pi$ system and a new $D^2\pi_g - X^2\pi$ (λ 5600-6800 Å) system has been completely analysed and observed by Brion *et al* (1973) and Malicet *et al* (1976).

The construction of potential energy curves is of considerable importance for understanding the kinetic mechanisms, spectral phenomena, stellar structure and many associated problems. Potential energy minima determine the possible structures and are thus related to bond strength and valence. The present paper deals with the construction of potential energy curves and dissociation energy of P_2^+ molecule. The rotational and vibrational constants required in the present study have been taken from Malicet *et al* (1976) and are presented in table 1.

2. Potential energy curves

In the construction of potential energy curves using the method of Lakshman and Rao (1971), the turning points for r_{\max} , r_{\min} are given in terms of f and g as follows :

$$r_{\max, \min} = [f/g + f^2]^{1/2} \pm f$$

Table 1. Molecular constants of P_2^+ .

State	T_e (cm ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	a_e (cm ⁻¹)	r_e (Å)
$X^3\Pi_u$	0	672.20	2.74	0.27600	0.00151	1.9858
$D^3\Pi_g$	18656.0	462.20	2.45	0.21960	0.00142	2.2262
$B^3\Sigma_u^+$	25305.0	410.50	3.23	0.24190	0.00211	2.1211
$C^3\Pi_g$	28648.5	441.47	2.58	0.21629	0.00136	2.2432

where f and g are

$$f = \left(\frac{h}{8\pi^2 \mu C \omega_e x_e} \right)^{1/2} X \ln W_i,$$

$$g = \left(\frac{2\pi^3 \mu C}{h} \right)^{1/2} \{ 2a_e (\omega_e x_e)^{-1} U_i^{1/2} \\ + (\omega_e x_e)^{-1/2} [2B_e - a_e \omega_e (\omega_e x_e)^{-1}] \ln W_i \},$$

$$\text{where } W_i = \frac{(\omega_i^2 - 4 (\omega_e x_e) U_i)^{1/2}}{\omega_i - 2 (\omega_e x_e)^{1/2} U_i^{1/2}}.$$

The other symbols have their usual spectroscopic significance. This method was successfully verified for several states belonging to different molecules in a number of cases (Ramakrishna Rao and Lakshman 1971, 1972, 1973; Lakshman *et al* 1977, 1978). Chakraborty and Pan (1973) suggested that this method is considered as reliable and accurate with less mathematical computations.

3. The method of curve fitting

The potential energy curves for molecular electronic states have been used to estimate the dissociation energy of diatomic molecules in a number of cases by comparing an empirical potential energy curve with a theoretical formula. The Lippincott potential function (Steele *et al* 1962) has been shown to fit to the RKR curves to a good extent (Ramakrishna Rao and Lakshman 1971a, b; Lakshman *et al* 1977).

Using the Lippincott potential function

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

$$\text{in which } a = \frac{F}{1 + 5/4 F}, \quad n = \frac{2F^2}{r_0(ab)^2},$$

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

The ground state $X^2\pi_g$ dissociation energy is evaluated as 4.03 eV. The RKR turning points are used in the above expression and for a particular value of D_0 , the observed energy values U are compared with calculated energy values. This procedure is repeated for different values of D_0 with variation of 0.06 eV and the value for which the best fitting of the energy values obtained is taken to be the dissociation energy of the molecule. Such a procedure has been employed for ground states of CO^+ (Bagare and Murthy 1978), MgO (Murthy and Bagare 1977) and TiO (Lakshman *et al* 1978). The average error of this function in the present case for the ground state is only 0.07% as measured by $V - V_{RKR}/D_0$ throughout the range of r values. Using this function for the molecules H_2 , C_2 , N_2 , O_2 and I_2 , Jagadish Singh *et al* (1970) found that the average error is only 1 to 2%. Employing the three parameter Lippincott function for P_2^+ molecule the dissociation energy for P_2^+ molecule is estimated as 4.03 ± 0.28 eV which is in very good agreement with the value of 4.5 ± 1.0 eV proposed by Gaydon (1968).

4. Results and discussion

The most prominent feature of these curves is that these 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 upper states to be nearly the same. This is evident from the approximately equal r_0 values for all these states. The potential energy curves have been constructed for eleven vibrational levels belonging to the ground state along with the turning points for the extrapolated energy value for the highest bound level have been presented in table 2. The calculations are carried out for various values of D_0 with a variation of 0.06 eV and these results are summarised in table 3. This value of D_0 is significant because it has been estimated by using the true potential energy curves based on experimental data. Having known the D_0 value for P_2^+ , the D_0 of P_2 (Gaydon 1968) and ionisation potential of phosphorous atom (Franklin *et al* 1969), the ionisation potential of P_2 is evaluated. The electron ionised from P_2 to give P_2^+ is antibonding since $D_0^0(P_2^+)$ is less than $D_0^0(P_2)$. The force constants for P_2^+ and P_2 are 0.41 and 0.55 M dynes/cm respectively, the P_2 bond is stronger than the P_2^+ bond, and as a consequence, the ionisation potential of P_2 must be greater than the ionisation potential of the phosphorous atom.

Ionisation potential of P_2 molecule is equal to

$$\begin{aligned} I(P) + D_0(P_2) - D_0(P_2^+), \\ = 10.98 + 5.03 - 4.03, \\ = 11.98 \pm 0.28 \text{ eV}, \end{aligned}$$

which is in good agreement with the value 11.80 eV given by Gaydon.

Table 2. Potential energy curves for different electronic states of P_3^+ .

v	U (cm $^{-1}$)	r_{\min} (Å)	r_{\max} (Å)
$X^3\Sigma_g^-$ state; $Te = 0$			
0	335.4	1.931	2.045
1	1002.1	1.894	2.092
2	1663.4	1.870	2.127
3	2319.1	1.851	2.156
4	2969.4	1.836	2.182
5	3614.2	1.822	2.207
6	4253.5	1.810	2.230
7	4887.4	1.799	2.251
8	5515.7	1.789	2.273
9	6138.6	1.780	2.293
10	6756.0	1.771	2.313
.	.		
.	.		
122	41226.2 (extrapolated)	1.048	8.498
$D^3\Pi_g$ state; $Te = 18656.0$			
0	230.5	2.160	2.298
1	687.8	2.116	2.355
2	1140.2	2.088	2.398
.	.		
.	.		
94	21798.6 (extrapolated)	1.021	10.121
$B^3\Sigma_g^+$ state; $Te = 25305.0$			
0	204.4	2.052	2.198
1	608.5	2.006	2.261
2	1006.1	1.977	2.308
3	1397.2	1.954	2.348
4	1781.8	1.935	2.385
.	.		
.	.		
63	13041.6 (extrapolated)	0.971	8.760
$C^3\Pi_g$ state; $Te = 28648.5$			
0	220.1	2.175	2.316
1	656.4	2.130	2.375
2	1087.5	2.101	2.419
3	1513.5	2.078	2.456
.	.		
.	.		
85	18884.4 (extrapolated)	0.952	9.760

Table 3. Comparison of the observed and calculated energy values.

r (Å)	U (cm ⁻¹)	$D_0 = 3.96$ eV	$D_0 = 4.03$ eV	$D_0 = 4.09$ eV
2.045	335.4	325.1	330.2	335.3
2.092	1002.1	972.1	987.3	1002.5
2.127	1663.3	1628.5	1653.9	1679.4
2.156	2319.1	2264.3	2299.7	2335.1
2.182	2969.4	2893.9	2939.1	2984.4
2.207	3614.2	3544.4	3599.8	3655.2
2.230	4253.5	4176.1	4241.3	4306.6
2.251	4887.4	4776.4	4851.4	4925.7
2.273	5515.7	5425.7	5510.5	5595.3
2.293	6138.6	6031.0	6125.3	6219.5
2.313	6756.1	6648.2	6752.1	6856.0
1.931	335.4	335.1	340.3	345.5
1.894	1002.1	999.8	1015.5	1031.1
1.870	1663.4	1656.3	1682.2	1708.0
1.851	2319.1	2317.0	2353.2	2389.4
1.836	2969.4	2934.4	2980.2	3026.0
1.822	3614.2	3591.8	3648.0	3704.1
1.810	4253.5	4221.5	4287.5	4353.5
1.799	4887.4	4855.8	4931.6	5007.5
1.789	5515.7	5479.7	5565.4	5651.0
1.780	6138.6	6083.2	6178.2	6273.3
1.771	6756.0	6727.1	6832.1	6937.3
Average % deviation		0.15	0.07	0.2

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