

Universal relation between spectroscopic constants

SARVPREET KAUR and C G MAHAJAN*

Department of Physics, Centre for Advanced Study in Physics, Panjab University,
Chandigarh 160 014, India

*Corresponding author. Email: cgm@pu.ac.in

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Abstract. A universal relation between the Sutherland parameter, $\Delta (= k_e r_e^2 / 2D_e)$ and the dimensionless parameter $G (= 8\omega_e x_e / B_e)$, has been established using 40 electronic states, which include ground as well as excited states of polar and non-polar molecules. This relation is used to predict the dissociation energy of four lowest electronic states of S_2 molecule. The respective values for the states $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$ and $B^3\Sigma_u^-$ turn out to be 36557, 31431, 28247 and 13429 cm^{-1} , and are in good agreement with the experimental values. Furthermore, metastable states $a^1\Delta_g$ and $b^1\Sigma_g^+$ of S_2 are shown to dissociate into $^3P_1 + ^3P_1$ as against the dissociation of $X^3\Sigma_g^-$ into $^3P_2 + ^3P_1$. In addition, a relation between Sutherland parameter Δ and internuclear distance r_e , viz., $\Delta = 2.2r_e$ has been obtained for the ground state of alkali diatomic molecules.

Keywords. Sutherland parameter; dissociation energy; alkali diatomic molecules; S_2 molecule.

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1. Introduction

The search for universal scaling properties of potential energy curves has been a topic of enduring yearn. Varshni [1], employing dimensionless parameters F and G , defined as

$$F = \alpha_e \omega_e / 6B_e^2 \quad \text{and} \quad G = 8\omega_e x_e / B_e \quad (1)$$

and treating both of these as a function of Sutherland parameter $\Delta (= k_e r_e^2 / 2D_e)$, made an unsuccessful effort to obtain a three-parameter universal potential function for the diatomic molecules. Following his futile attempt which was further pursued by Graves and Parr [2], several approaches [3–7] aimed at universal potential energy curve, including the concept of reduced potentials/scaled potentials [8,9], have been proposed. The main conclusion of all these endeavours was: the concept of a single reduced potential energy curve is valid for related systems [5,9] only. Recently, Szentpaly [10] tackled this problem of universal potential curve by revoking the idea of valence state [11] and thereby the valence state dissociation energy, D_{VS} which refers to an asymptote in which atoms are in suitable valence state. He has introduced a new dimensionless parameter z analogous to Sutherland parameter and equal to $k_e r_e^2 / D_{VS}$. He found that F and G are related to z through

$$F = \frac{22}{3}z, \quad (2)$$

$$G = \frac{2}{3}z^2 + 6z + 3. \quad (3)$$

He has, on the basis of his studies on 25 molecules, shown that his universal three-parameter valence state potential energy curve reveals greater similarity near the minimum of potential energy curve and the values of α_e and $\omega_e x_e$ may be predicted more accurately.

In the present investigations the problem is treated in a somewhat different manner, where the aim has been to find a universal relation between G and Δ . The functional dependence of Δ on G leads to a very important and reliable analytical technique to predict the dissociation energy, D_e – the main motive of the present studies. The study is based on 40 electronic states, the constants for which are taken from the literature and are given in table 1. The accuracy of this approach is demonstrated by predicting the dissociation energy of four electronic states of S_2 molecule.

2. Universal relation between spectroscopic constants

Recalling the fact that, (i) for a given value of r_e and hence $B_e (= h/8\pi^2\mu r_e^2)$ of a molecule, G depends on anharmonicity $\omega_e x_e$, (ii) Δ is governed by the dissociation energy, D_e and (iii) the nature of the outer limb of the potential energy curve is guided by the anharmonicity and dissociation energy, an attempt has been made to seek their dependence on each other. In this context, it may be mentioned that G does not vary linearly with Δ and the departure is more for large values of Δ (figure 1). Therefore, a graph of $\ln G$ vs. $\ln \Delta$ has been plotted for the experimental data pertaining to 40 electronic states (figure 2), and is found to be described by

$$\ln G = 1.91578 (\pm 0.09727) + 0.97111 (\pm 0.03809) \ln \Delta \quad (4)$$

with correlation coefficient as 0.97.

When G , k_e (i.e. ω_e) and r_e are known, dissociation energy through Δ can be predicted accurately using (4). From the graph between $\ln G$ and $\ln \Delta$ and the molecular constants given in table 2, dissociation energy of the four lowest electronic states $X^1\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$ and $B^3\Sigma_u^-$ of S_2 have been found to be 36557, 31431, 28247 and 13429 cm^{-1} , respectively. These values match well with the corresponding experimental data (table 2) [12,13]. In order to reinforce the reliability of the method, the predicted value of D_e supplemented with the experimental data for ω_e , r_e , the vibronic states and hence the bands expected from the transitions among these states have been obtained numerically employing the fourth-order Runge–Kutta method (figure 3) using analytical potential function U_I of Kaur and Mahajan [14]. The calculated values of bands are in good agreement with the experimental values implying that the D_e values obtained from graph or eq. (4) are fairly close to the actual values.

3. Discussion and conclusion

In most of the earlier works on reduced/scaled potential energy curves for diatomic molecules, emphasis has been on constructing F and G as a function of Δ [1–7] or as a

Table 1. Molecular constants used for 40 electronic states of diatomic molecules.

Molecular state	r_e (Å)	D_e (cm ⁻¹)	ω_e (cm ⁻¹)	α_e 10 ³ (cm ⁻¹)	B_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	μ_e (a.m.u.)	Ref.
Li ₂ X ¹ Σ _g ⁺	2.6729	8516.780	351.430	7.040	0.6726	2.6100	3.5080	[22,12]
Na ₂ X ¹ Σ _g ⁺	3.0788	6022.600	159.177	0.873	0.1547	0.7254	11.4949	[12,23]
K ₂ X ¹ Σ _g ⁺	3.9244	4440.000	92.405	0.212	0.0562	0.3276	19.4800	[24]
Rb ₂ X ¹ Σ _g ⁺	4.2099	3950.000	57.7807	0.055	0.0224	0.1391	42.4559	[25]
Cs ₂ X ¹ Σ _g ⁺	4.6480	3649.500	42.020	0.022	0.0117	0.0826	66.4527	[26]
Cl ₂ X ¹ Σ _g ⁺	1.9872	20276.440	559.751	1.516	0.2442	2.6943	17.4844	[27]
Cl ₂ B ³ Π	2.4311	3341.170	255.3800	2.511	0.1631	4.8000	17.48442	[28]
I ₂ XO _g ⁺	2.6664	12547.335	214.520	0.113	0.0373 ₇	0.6079	63.4522	[29]
IClX ¹ Σ ⁺	2.3209	17557.600	384.275	0.532	0.1142	1.4920	27.4147	[30]
IClA ³ Π ₁	2.6850	3814.700	211.030	0.744	0.0852 ₉	2.1200	27.4147	[31]
IClA ³ Π ₂	2.6651	4875.520	224.571	0.674	0.0865	1.8823	27.4147	[30,31]
HF ₂ X ¹ Σ ⁺	0.9168	49384.000	4138.320	772.400	20.9557	89.8800	0.9571	[32]
H ₂ X ¹ Σ _g ⁺	0.7416	38297.000	4401.265	3051.300	60.8477	120.6020	0.5039	[33]
COX ¹ Σ ⁺	1.1283	90529.000	2169.813	17.504	1.93137	15.2883	6.8562	[12]
XeOd ¹ Σ ⁺	2.8523	693.000	156.832	5.400	0.1456	9.8678	14.2327	[34]
Ar ₂ XO _g ⁺	3.7610	99.500	30.6800	3.641	0.0596 ₅	2.4200	19.9810	[35]
O ₂ X ³ Σ _g ⁻	1.2075	42047.000	1579.247	15.466	1.4456	11.5008	7.9975	[36]
O ₂ b ₁ Σ _g ⁺	1.2268	28852.000	1432.775	18.198	1.4004	14.0065	7.9975	[36]
O ₂ A ³ Σ _u ⁺	1.5215	6643.000	815.648	18.053	0.9105	19.8513	7.9975	[36]
O ₂ B ³ Σ _u ⁻	1.6042	8121.000	709.050	11.922	0.8189	10.6100	7.9975	[36]
O ₂ ⁺ X ² Π _g	1.1171	54681.000	1905.335	18.970	1.6905	16.3040	7.9973	[36]
NOX ² Π _{1/2}	1.1507 ₇	53323.758	1904.204	17.100	1.6719 ₅	14.0750	7.4664	[12]
NOB ² Π	1.4167	26544.888	1037.200	12.000	1.0920	7.7000	7.4664	[12]
N ₂ X ¹ Σ _g ⁺	1.0976	78742.304	2358.570	17.318	1.9982	14.3240	7.0015	[12]
N ₂ A ³ Σ _u ⁺	1.2866	29772.23	1460.640	18.000	1.4546	13.8720	7.0015	[12]
N ₂ a ¹ Π _g	1.2203	48974.915	1694.208	17.930	1.6169	13.9490	7.0015	[12]
N ₂ B ³ Π _g	1.2126	39534.94	1733.390	17.910	1.6374	14.1220	7.0015	[12]
OHX ² Π _i	0.9696	37308.074	3737.76	724.200	18.9108	84.8813	0.9481	[12]
OHA ² Σ ⁺	1.0121	20412.938	3178.860	786.800	17.3580	92.9170	0.9481	[12]
Br ₂ X ¹ Σ _g ⁺	2.2810	15900.307	325.321	0.318	0.0821	1.0774	39.4591	[12]
C ₂ X ¹ Σ _g ⁺	1.2425	50104.485	1854.710	17.650	1.8198	13.3400	6.0000	[12]
COd ³ Δ _i	1.3696	28368.336	1171.940	17.820	1.3108	10.6350	6.8562	[12]
COA ¹ Π	1.2353	25617.027	1518.240	23.530	1.6115	19.4000	6.8562	[12]
COe ³ Σ ⁻	1.3840	25391.113	1117.720	17.530	1.2836	10.6860	6.8562	[12]
ZnHΣ ⁺	1.594	7670.453	1607.6	250.00	6.6794	55.14	0.9928	[1]
CdHa ³ Σ ⁺	1.762	6184.712	1430.700	218.00	5.437	46.30	0.9992	[1]
HgHa ³ Σ ⁺	1.740	3726.94	1387.100	312.00	5.549	83.01	1.0031	[1]
HClA ³ Σ ⁺	1.275	37239.14	2989.7	301.9	10.591	52.05	0.9799	[1]
HBrA ³ Σ ⁺	1.414	31613.54	2649.7	226	8.473	45.21	0.9956	[1]
HIa ³ Σ ⁺	1.604	25811.60	2309.5	183	6.551	39.73	1.0002	[1]

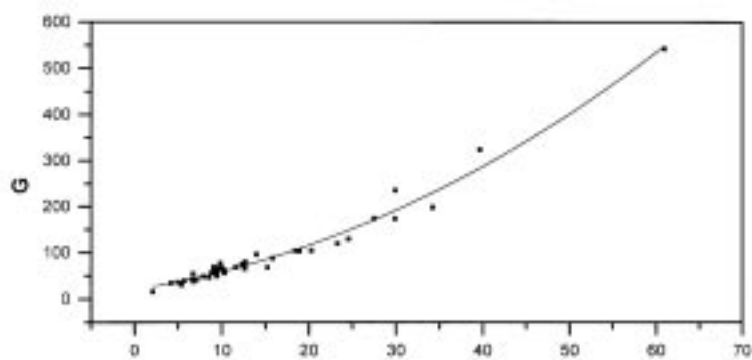


Figure 1. Graph of G vs. Δ .

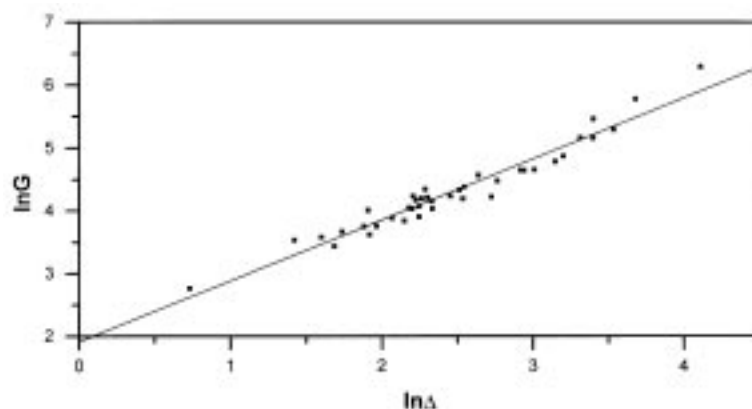


Figure 2. Graph of $\ln G$ vs. $\ln \Delta$.

Table 2. Molecular constants of S_2 molecule.

Molecular state	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	α_e (10^3 cm^{-1})	B_e (cm^{-1})	D_e^\dagger (cm^{-1})	Ref.
$X^3\Sigma_g^-$	1.8892	725.65	2.844	1.57	0.2954_7	36556 (35999)*	[12] [17]
$a^1\Delta_g$	1.8983	702.35	3.090	1.73	0.2926_2	31430	[12]
$b^1\Sigma_g^{+\ddagger\dagger}$	1.9100	693.00	3.274	1.83	0.2890_6	28821	[12,37]
$B^3\Sigma_u^-$	2.170	434.00	2.750	2.30	0.2239	13428 (13403)*	[12] [13]

*Values in bracket are the experimental values taken from literature.

\dagger Dissociation energy is calculated using eq. (4).

$\ddagger\dagger$ ω_e and $\omega_e x_e$ are taken from constants tables [12] and those of r_e , α_e and B_e from the high resolution studies of Fink *et al* [37].

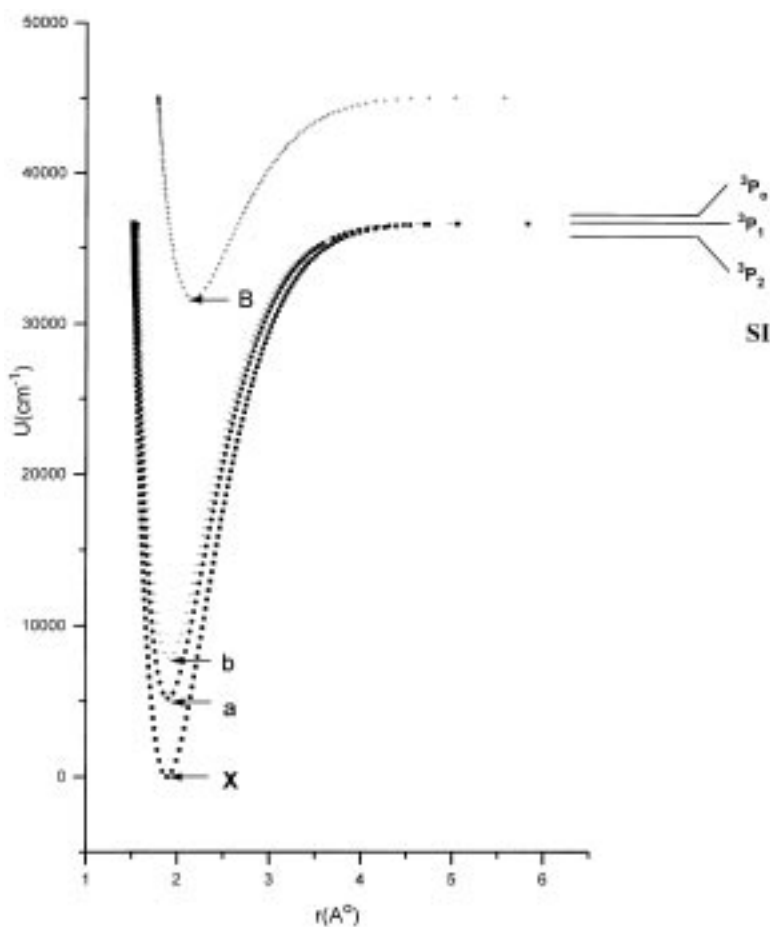


Figure 3. Potential energy curves of various electronic states of S₂ molecule.

function of parameter z [10] to compare the observed experimental data. In addition Freeman *et al* [15], using the observed data of 23 electronic states as given in [16], obtained the following relation between F and G ,

$$G = 27.4F^{4/3}. \quad (5)$$

They concluded that the above equation provides better correspondence for homonuclear molecules while polar molecules tend to follow the alternate relation obtained using eqs (2) and (3). In the present studies, corresponding relation between G and Δ has been obtained for 40 electronic states which include, as stated earlier, ground as well as excited states of polar and non-polar molecules. The relation leads to a very important conclusion that, contrary to the findings of Freeman *et al* [15], all molecules considered in the present studies, irrespective of their bonding nature, follow the same model within a deviation as given by eq. (4). It is a major improvement over their findings. Therefore, eq. (4) is taken as a universal relation between G and Δ . Inverting this expression, we get

$$\ln \Delta = 1.02975 \ln G - 1.97277. \quad (6)$$

(standard deviations are not included)

Thus, if G is known for some electronic state of a molecule, corresponding Δ can be obtained from the graph, i.e., eq. (6) for that state. And Δ , in turn, yields the value of D_e . The calculated D_e for the ground state, $X^3\Sigma_g^-$ is 36557 cm^{-1} which compares well with the experimental value of 35999 cm^{-1} obtained from the pre-dissociation limit in $B^3\Sigma_u^-$ assuming dissociation at this limit into $^3P_2 + ^3P_1$ [17]. The values also compare well with the values 35686 and 35928 cm^{-1} , obtained respectively from photoionization mass-spectrometry [18] and thermal measurements [19]. The D_e values for $a^1\Delta_g$ and $b^1\Sigma_g^+$ are 31431 and 28247 cm^{-1} , respectively. These values together with the fact that all the lowest three states arise from the electronic configuration $(\pi_u 3p)^4 (\pi_g 3p)^2$ or, alternatively, if expressed in separate atom model, from $^3P + ^3P$, have enabled us to express the minimum energy of the states $a^1\Delta_g$ and $b^1\Sigma_g^+$ with respect to the minimum of $X^3\Sigma_g^-$. The values are $5126(36557-31431) \text{ cm}^{-1}$ and $8310(36557-28247) \text{ cm}^{-1}$, respectively. These are quite close to the ones obtained for the (0,0) bands at 5730 ± 20 and $7980 \pm 15 \text{ cm}^{-1}$ for $a-X$ [20] and $b-X$ [37] band system, respectively. (The difference between the zero point energy of the states X , 'a' and 'b' are well within the accuracy of (0,0) bands. That is why the calculated separation between the minima is compared with (0,0) band of the system.) Knowing that the dissociation limit of $X^3\Sigma_g^-$ to $S(^3P_2) + S(^3P_1)$ is 35999 cm^{-1} [17] and that the spin components 3P_1 and 3P_0 lie about 396 and 573 cm^{-1} , respectively, above 3P_2 , the deviation of the values can be explained by considering the molecular electronic states resulting from the identical states of the separated like atoms. The possible combinations are $S(^3P_2) + S(^3P_2)$, $S(^3P_2) + S(^3P_1)$, $S(^3P_2) + S(^3P_0)$, $S(^3P_1) + S(^3P_1)$, $S(^3P_1) + S(^3P_0)$ and $S(^3P_0) + S(^3P_0)$. For the molecular electronic state $a^1\Delta_g$, $S(^3P_0) + S(^3P_0)$ and $S(^3P_0) + S(^3P_1)$ do not lead to $\Omega = 2$, and therefore, are not feasible. Dissociation of $^1\Delta$ into $S(^3P_1) + S(^3P_1)$ yields $D_e = 30665(35999 + 396 - 5730) \text{ cm}^{-1}$ which compares well with the analytically predicted value 31431 cm^{-1} . Other combinations yield a value less than 30665 cm^{-1} . On the other hand, $b^1\Sigma_g$ has heat of dissociation, $D_e = 28414(35999 + 396 - 7980) \text{ cm}^{-1}$, if the state dissociates into $^3P_1(S) + ^3P_1(S)$ and has $D_e = 28592 \text{ cm}^{-1}$ corresponding to dissociation into $^3P_1(S) + ^3P_0(S)$. Again, dissociation limit of $^3P_1(S) + ^3P_1(S)$ provides D_e value close to the analytical value 28247 cm^{-1} . Therefore, it is believed that both $a^1\Delta_g$ and $b^1\Sigma_g^+$ dissociate into $^3P_1(S) + ^3P_1(S)$. This observation is supported by the fact that both the states $a^1\Delta_g$ and $b^1\Sigma_g^+$ of S_2 are observed simultaneously in a discharge flow system $O_2(^1\Delta_g)$ sensitized chemiluminescence [20]. The above findings not only reinforce our conclusion that D_e can be predicted accurately from the analytical relation (6) but also leads to the fact that both the states $a^1\Delta_g$ and $b^1\Sigma_g^+$ dissociate into $^3P_1(S) + ^3P_1(S)$.

4. Relation for alkali group atoms

In addition to the above, a relation between Δ and r_e for the ground electronic states of alkali group diatomic molecules has been obtained. It has been found that the Sutherland parameter Δ varies linearly with the internuclear distance r_e expressed by the relation

Table 3. Molecular constants of alkali group molecules.

Molecular state	r_e (Å)	ω_e (cm ⁻¹)	μ (a.m.u)	D_e (cm ⁻¹)	D_e^* (cm ⁻¹)	Ref.
Li ₂ X ¹ Σ _g ⁺	2.6729	351.430	3.508	8516.780	7805.09	[22]
LiNaX ¹ Σ _g ⁺	2.8850	256.990	5.375	7067.81	6903.00	[38]
LiKX ¹ Σ _g ⁺	3.3169	211.910	5.945	6150.00	5968.00	[38]
Na ₂ X ¹ Σ _g ⁺	3.0788	159.177	11.4949	6022.600	6043.73	[23]
NaKX ¹ Σ _g ⁺	3.4968	124.0124	14.4587	5274.90	5240.00	[38]
NaCsX ¹ Σ _g ⁺	3.8500	98.8851	19.599	4950.00	4972.00	[38]
K ₂ X ¹ Σ _g ⁺	3.9244	92.405	19.4800	4440.000	4399.10	[24]
KRbX ¹ Σ _g ⁺	4.07	75.5	26.708	4071.00	4176.260	[12]
KCsX ¹ Σ _g ⁺	4.28	66.2	30.1304	3824.000	3809.102	[12]
Rb ₂ X ¹ Σ _g ⁺	4.2099	57.780	42.4559	3950.000	4021.92	[25]
RbCsX ¹ Σ _g ⁺	4.4271	50.0116	51.810	3833.00	3866.63	[38]
Cs ₂ X ¹ Σ _g ⁺	4.6480	42.020	66.4527	3649.500	3675.77	[26]

*Dissociation energy as calculated using relation $\Delta = 2.2r_e$.

$\Delta = 2.2r_e$. That means if r_e and ω_e are known for any ground state of alkali group diatomic molecule then corresponding D_e of that state can be predicted analytically. The preceding relation is used to predict the dissociation energy of ground states of Li₂, Na₂, K₂, Rb₂, Cs₂, LiK, NaK, NaCs, RbCs, KRb and KCs (column 7 of table 3). The errors are less than 1% except for Li₂ where the deviation is 8% and LiK, LiNa for which the differences are 2.9% and 2.3% respectively. The relative large deviations in these molecules may possibly be attributed to Li atom where only K shell is completely filled; a situation analogous to the one that one finds in the analytical relation $r_e^3\omega_e n^{1/2} = \text{constant}$ [21] between r_e and ω_e values of the electronic states of different molecules, where n is the number of electrons outside the closed atomic shells. The value of constant for molecule having only K closed shells is found to be different from others.

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