

Dissociation energy of diatomic molecules

SARVPREET KAUR and C G MAHAJAN

Centre of Advanced Study in Physics, Panjab University, Chandigarh 160 014, India
E-mail: spectphys@ch1.vsnl.net.in

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Abstract. The dissociation energy of twelve diatomic molecules has been determined by fitting four-parameter potential function $U(r) = D_e[1 - \exp\{-b(r - r_e)\}]/[1 - C \exp\{-b(r - r_e)\}]^2$ to the true Rydberg–Klein–Rees (RKR) curves for their fifteen electronic states using the mean square deviation as the criterion for the selection of the best fit. Average deviation of D_e has been found to be 2.7% as compared to 20.5% obtained with Lippincott's potential function for these molecules. In addition the anharmonicity constant $\omega_e x_e$ has also been calculated for the same electronic states yielding average mean deviation 8.9%.

Keywords. Dissociation energy; four-parameter potential; anharmonicity constant.

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1. Introduction

The spectroscopic data for most of the diatomic molecules is available for vibrational levels which are considerably below the dissociation limit. So different extrapolation methods have been employed to find the dissociation energy of these molecules and Birge–Sponer [1] approach is most commonly used for this purpose. Obviously, the results inherently suffer from an uncertainty determined by the extrapolation gap and the method of extrapolation. In addition, it has long been known [2] that vibrational energies near the dissociation limit and hence the vibrational spacings depend on the functional form of the long range potential. This, in turn, leads to a marked deviation of graphical extrapolation from the accurate estimate of the dissociation limit. Using asymptotic approximation for long range potentials of the form

$$V(r) = D_e - \sum_n \frac{C_n}{r^n}, \quad (1)$$

where D_e is the dissociation limit of the potential and C_n is given by

$$E(v) = D_e - \frac{C_n}{(r_{\max}(v))^2}. \quad (2)$$

LeRoy and co-workers [2–4] have developed WKB based extrapolation technique to estimate the dissociation limits. Their near-dissociation expansion (NDE) formalism has led to results far better than the Birge–Sponer extrapolation method. It may, however,

Table 1. Experimental molecular constants used in this work.

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	[19]
Na ₂ X ¹ Σ _g ⁺	3.0788	6022.600	159.177	0.873	0.1547	0.7254	11.4949	[20]
K ₂ X ¹ Σ _g ⁺	3.9244	4440.000	92.405	0.212	0.0562	0.3276	19.4800	[11]
Cl ₂ X ¹ Σ _g ⁺	1.9872	20276.440	559.751	1.516	0.2442	2.6943	17.4844	[21]
Cl ₂ B ³ Π	2.4311	3341.170	255.3800	2.511	0.1631	4.8000	17.48442	[22]
I ₂ XO _g ⁺	2.6664	12547.335	214.520	0.113	0.0373 ₇	0.6079	63.4522	[23]
IClX ¹ Σ ⁺	2.3209	17557.600	384.275	0.532	0.1142	1.4920	27.4147	[16]
IClA ³ Π ₁	2.6850	3814.700	211.030	0.744	0.0852 ₉	2.1200	27.4147	[16, 17]
IClA ³ Π ₂	2.6651	4875.520	224.571	0.674	0.0865	1.8823	27.4147	[17]
HFX ¹ Σ ⁺	0.9168	49384.000	4138.320	772.400	20.9557	89.8800	0.9571	[24]
H ₂ X ¹ Σ _g ⁺	0.7416	38297.000	4401.265	3051.300	60.8477	120.6020	0.5039	[25]
COX ¹ Σ ⁺	1.1283	90529.000	2169.813	17.504	1.93137	13.2883	6.8562	[13, 14]
XeOd ¹ Σ ⁺	2.8523	693.000	156.832	5.400	0.1456	9.8678	14.2327	[26]
Cs ₂ X ¹ Σ _g ⁺	4.6480	3649.500	42.020	0.022	0.0117	0.0826	66.4527	[27]
Rb ₂ X ¹ Σ _g ⁺	4.2099	3950.000	57.7807	0.055	0.0224	0.1391	42.4559	[12]

be pointed out that a proper RKR analysis yields a much more accurate estimate of D_e [5].

In 1990, Wei Hua introduced a four-parameter (FP) potential function [6],

$$U(r) = D_e \left[\frac{1 - \exp\{-b(r - r_e)\}}{1 - C \exp\{-b(r - r_e)\}} \right]^2, \quad (3)$$

where $b = (1 - C)a$, and C is an adjustable parameter having $|C| < 1$ with $a = \sqrt{k_e/2D_e}$.

The FP potential fits very closely to the RKR curves compared to Morse and other analytical functions [6], when the potential domain extends to near dissociation limit. It is, therefore, natural to expect that FP potential would predict the dissociation limit precisely. We have made an attempt to investigate this aspect of the FP potential and the results constitute the content of this communication. Wei Hua considered fifteen electronic states of twelve molecules to examine his FP potential and the same electronic states have been used in the present studies as the spectroscopic constants, the RKR potential curves and the dissociation energies are known very accurately for these states. The molecular constants and respective dissociation energies are given in table 1.

2. Estimation of the dissociation energy

Because of the anharmonicity the molecules in the highly excited vibrational levels spend most of their time in the neighborhood of outer turning points. Therefore, the vibrational spacings [2], rotational constants [7] and other properties [8] of the diatomic molecules near the dissociation limit, are explained mainly by the outer limb of the potential curve.

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Accordingly, we have used the outer turning points, i.e. r_{\max} , obtained from the RKR potential curve, corresponding to experimentally observed vibrational levels. Since C in the FP potential function (eq. (3)) is an adjustable constant, C and D_e have been evaluated by using iteration method such that mean square deviation, given by

$$\Delta Y_j = \frac{\sqrt{(U_j - U_{\text{RKR}})^2}}{D_e}, \quad (4)$$

where j stands for various potential functions, has minimum value. With the rough estimated values of D_e from the linear extrapolation method, i.e., $D_e = \omega_e^2/4\omega_e x_e$ and C from the relation [9]

$$C_{\text{rel}} = \left(-\frac{1}{12} + x\right) - \sqrt{\frac{120}{144} - \frac{37}{48}x^2 - \frac{2}{12}x + \frac{17}{144} \frac{G}{ar_e^2}}, \quad (5)$$

where

$$x = \frac{1 + F}{ar_e}, \quad F = \frac{\alpha_e \omega_e}{6B_e^2}, \quad \text{and} \quad G = \frac{8\omega_e x_e}{B_e}$$

for the whole potential curve as the starting points, the potential energies corresponding to FP potential have been obtained by changing D_e and C in steps of $\pm 100 \text{ cm}^{-1}$ and ± 0.1 , respectively. The resulting values are correlated with the experimental results and the values of D_e and C corresponding to minimum value of Y_j are chosen for the second scan. In the second and subsequent scans, the values of D_e and C are varied in steps of decreasing magnitudes. The process is continued till Y_j is minimum. The last scan has been carried out by changing D_e by $\pm 1 \text{ cm}^{-1}$ and C by ± 0.001 . The value of D_e that corresponds to minimum deviation Y_j in the final scan is regarded as the best estimate of D_e and relevant C value.

3. Results and discussion

Dissociation energies of fifteen electronic states of molecules Li_2 , Na_2 , K_2 , Rb_2 , Cs_2 , Cl_2 , I_2 , ICl , HF , H_2 , CO , XeO have been obtained employing the molecular constants listed in table 1 and the results are presented in table 2. For comparison, values of D_e obtained from Lippincott's analytical potential function [10]

$$U(r) = D_e(1 - e^{-x})\{1 - abx^{1/2} \exp[-bx^{1/2}]\}, \quad (6)$$

where

$$F = \frac{\alpha_e \omega_e}{6B_e^2}, \quad a = \frac{F}{1 + (5F/4)}, \quad N = \frac{2}{r_e} \left(\frac{F}{ab}\right)^2 \quad \text{and} \\ x = \frac{N(r - r_e)^2}{2r}, \quad b = 1.065;$$

which is considered to be best among the three parameter potential functions for the prediction of D_e are also included in table 2. Furthermore, anharmonicity constant $\omega_e x_e$

Table 2. Comparison of experimental values of D_e with calculated values and the mean deviations $\Delta X = (D_e(\text{exptl}) - D_e(i))/(D_e(\text{exptl}))$ where $D_e(i)$ stands for, $D_e(\text{FP})$, FP; $D_e(\text{Lipp})$, Lippincot; for fifteen electronic states.

State	$D_e(\text{exptl})$ (cm^{-1})	C_{min}	$D_e(\text{FP})$ (cm^{-1})	$D_e(\text{Lipp})$ (cm^{-1})	ΔX_{FP} (%)	ΔX_{Lipp} (%)	$C_{\text{min}}(1/3)$	$D_e(\text{FP}_{1/3})$ (cm^{-1})	$\Delta X_{\text{FP}}(1/3)$ (%)	E_{max}/D_e
*Li ₂ X ¹ Σ _g ⁺	8516.78	-0.350	8613	10111	1.1	18.7	-0.472	8514	0.03	0.9998
*Na ₂ X ¹ Σ _g ⁺	6022.00	-0.482	6015	7032	0.1	16.7	-0.489	6013	0.15	0.9961
**K ₂ X ¹ Σ _g ⁺	4440.00	-0.359	4646	8130	4.6	83.1	-0.391	4580	3.15	0.8306
*Cl ₂ X ¹ Σ _g ⁺	20276.40	-0.349	20574	23213	1.5	14.5	-0.509	20283	0.03	0.9995
*Cl ₂ B ³ Π	3341.17	+0.018	3282	3300	1.8	1.3	+0.228	3327	0.42	0.9990
*I ₂ XO ⁺	12547.00	-0.368	12497	14102	0.4	12.4	-0.346	12492	0.44	0.9997
**IClX ¹ Σ ⁺	17557.00	-0.316	17831	20067	1.6	14.2	-0.458	17548	0.05	0.9970
*IClA ³ Π ₁	3814.00	-0.248	3719	4125	2.5	8.3	-0.030	3766	1.25	0.9934
**IClA ³ Π ₂	4875.00	-0.288	4746	5338	2.6	9.5	-0.191	4780	1.95	0.9853
++HF ¹ Σ ⁺	49384.00	+0.000	51387	48468	4.0	1.9	-0.110	50261	1.77	0.9928
+H ₂ X ¹ Σ _g ⁺	38297.00	-0.009	39983	38109	4.4	0.5	-0.134	38860	1.47	0.9922
+COX ¹ Σ ⁺	90529.00	+0.069	95712	78612	5.7	13.2	+0.077	96250	6.31	0.6995
**XeOd ¹ Σ ⁺	693.00	+0.196	660	619	4.8	10.7	+0.368	687	0.86	0.9476
*Cs ₂ X ¹ Σ _g ⁺	3649.50	-0.450	3658	5055	0.24	38.5	-0.450	3635	0.40	0.9944
**Rb ₂ X ¹ Σ _g ⁺	3950.00	-0.370	4172	6447	5.6	63.2	-0.390	4131	4.58	0.8388
Average					2.7	20.5			1.5	

D_e values are derived from: *NDE long range technique; **RKR potential curve; +Extrapolation from the RKR curve; ++Limiting curve of dissociation.

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Table 3. Comparison of experimental values of $\omega_e x_e$ with calculated values and the mean deviations [$\Delta X = (\omega_e x_e(\text{exptl}) - \omega_e x_e(i)) / (\omega_e x_e(\text{exptl}))$]; where $\omega_e x_e(i)$ stands for $\omega_e x_e(\text{FPC}_{\text{rel}})$, FP; $\omega_e x_e(\text{FPC}_{\text{min}})$, FP; using equation (7) for the corresponding electronic states given in table 1.

$\omega_e x_e(\text{exptl.})$ cm^{-1}	$\omega_e x_e(\text{FPC}_{\text{rel}})$ cm^{-1}	$\omega_e x_e(\text{FPC}_{\text{min}})$ cm^{-1}	$\Delta X_{\text{FPC}_{\text{rel}}}$ (%)	$\Delta X_{\text{FPC}_{\text{min}}}$ (%)
2.6100	3.2150	2.7680	23.1	6.1
0.7254	0.8816	0.7895	21.5	6.4
0.3276	0.3859	0.3536	17.8	7.9
2.6943	3.5437	2.9418	31.5	9.2
4.8000	4.4261	5.0540	7.8	5.2
0.6079	0.7973	0.7063	31.2	16.2
1.4920	1.9104	1.6220	28.0	8.7
2.1210	2.4911	2.4340	17.4	14.7
1.8823	2.2354	2.1110	18.8	12.2
89.8800	98.4446	83.3050	9.5	7.3
120.6020	152.4790	120.2257	26.4	0.3
13.2883	13.6250	13.2027	2.5	0.6
9.8678	8.3081	11.5570	15.8	17.1
0.0826	0.0950	0.0911	15.1	10.3
0.1391	0.1678	0.1540	20.6	10.8
Average			17.4	8.9

have been computed for these electronic states using the relation

$$\omega_e x_e = \frac{\hbar}{8\pi^2 c \mu} a^2 (1 + C + C^2) = B_e \Delta (1 + C + C^2) \quad (7)$$

obtained in our earlier work [9]. Here, we have used C calculated above for the outer limb. These results together with the experimental values of $\omega_e x_e$ and the ones found by us in ref. [9], are compiled in table 3.

Earlier works on the studies of electronic states of the molecules subjected to the present analysis (see the references in table 1) show that the properly executed NDE method of LeRoy *et al* [2–4] and RKR approach yield accurate values of D_e . So we have taken these D_e values as experimental (being the best prediction) to compare our findings and have given these in the second column of the table 2. It may be mentioned that D_e for HF included in this table has been obtained earlier from the limiting curve of dissociation.

A comparison of our results constituting third column of table 2 with experimental values listed in column 2 shows that the extent of agreement depends on the method. For the electronic states $\text{Li}_2(\text{X}^1\Sigma_g^+)$, $\text{Na}_2(\text{X}^1\Sigma_g^+)$, $\text{Cl}_2(\text{X}^1\Sigma_g^+)$, $\text{I}_2(\text{X}^1\Sigma_g^+)$, $\text{ICl}(\text{X}^1\Sigma_g^+)$ and $\text{Cs}_2(\text{X}^1\Sigma_g^+)$ for which experimental D_e values have been found with NDE technique (that includes the long range forces) the difference is less than 2%. However, in A and A' electronic states of ICl the deviations are respectively 2.5% and 2.6%. The deviation in the case of the electronic state A can be viewed in the light of reported vibrational perturbations near dissociation and the merging approach (merging the constants from individual absorption band and emission band through least square fit) used to obtain D_e [16]. Similar explanation is valid for state A' also since there is a possibility of perturbation in state A' [17], near the dissociation limit, because there exists a shallow $\Omega = 2$ state [18], which converges to the same dissociation limit.

On the other hand, for the electronic states $K_2(X^1\Sigma_g^+)$, $HF(X^1\Sigma_g^+)$, $H_2(X^1\Sigma_g^+)$, $CO(X^1\Sigma_g^+)$, $XeO(X^1\Sigma_g^+)$, and $Rb_2(X^1\Sigma_g^+)$, whose D_e have been determined using RKR potential curves the percentage variations lie between 4 and 5.7. On referring back to literature, it is found that the highest observed vibrational levels in K_2 , CO and Rb_2 viz. $v = 37$ at 63334.333 cm^{-1} for CO [13,14], $v = 50$ at 3687.749 cm^{-1} for K_2 [11], $v = 72$ at 3313.143 cm^{-1} for Rb_2 [12], giving $E_{\max}/D_e \sim 0.70, 0.83,$ and 0.84 respectively, where E_{\max} denotes the energy of highest observed level, are fairly below the respective dissociation limits. That means, RKR potential curve has been drawn accurately only up to the observed levels. Moreover, since RKR does not provide any direct means of extrapolation beyond the observed levels [2], indirect methods have been employed to obtain D_e values which are likely to be at the variance from the accurate values. In the case of XeO and H_2 the levels are observed only up to $v = 8$ and $v = 14$, respectively, so that D_e are expected to be more erroneous.

Long range forces have dominant influence [2] on the vibrational levels close to dissociation limit (\sim top 10% of the potential well). With a view to examine the performance of the FP potential function close to the dissociation limit, D_e (denoted as D_e ($FP_{1/3}$) in table 2) and C (referred to as $C_{\min}(1/3)$ in table 2) have been derived considering only the highest one-third of the known vibrational levels. But for the CO electronic state, the results (given in column 10 of table 2) for all other states have been improved significantly. The slight adverse result of CO is understandable since the known data constitute only 70% of the potential well starting from equilibrium position. This observation, besides providing better accuracy of D_e , also strengthens the earlier findings [6], that FP potential describes experimental potential curves more accurately especially when the potential domain extends to near the dissociation limit.

Values of vibrational constant $\omega_e x_e$, when computed from the outer limb of the RKR curve show a marked improvement over the ones calculated using inner wall as well as the outer wall (i.e. $r_{\min} < r < r_{\max}$) of the potential curve (table 3). The average mean deviation from the experimental values has been reduced to 8.9% from 17% [9]. Furthermore, since $\omega_e x_e$ has been calculated using outer limb of the potential curve, the findings are in conformity with the fact that, because of anharmonicity, the vibrational spacings and other properties of diatomic molecules [2, 7, 8] are explained mainly by the outer limb of the potential curve.

4. Conclusion

FP potential function of Wei Hua can be used to predict dissociation energy of the electronic states of diatomic molecules. The accuracy of prediction is close to the one obtained by NDE long range expansion technique or by RKR potential curve constructed up to near dissociation limit. Besides, FP potential function, through equation (7), predicts $\omega_e x_e$ value better than the known three parameter analytical functions.

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