

Some new four-parameter potentials and their use in the study of vibrational thermodynamical quantities of diatomic molecules

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Abstract. Three four-parameter potentials, U_I , U_{II} and U_{III} have been proposed and their accuracy has been demonstrated by finding the mean square deviation from the true RKR potential curve for 15 electronic states of 12 diatomic molecules. Their percentage average mean square deviations from RKR curve have been found to be 1.45, 1.86 and 2.89, respectively. These compare favourably with the value 2.67 for the recently suggested four-parameter potential of Wei Hua which itself yields better results than the commonly employed three-parameter potentials. The superiority of the new potentials (especially of U_I and U_{II}) has been further established by using these potentials to calculate the molecular constants α_e and $\omega_e x_e$ following Dunham's method. The corresponding percentage average mean deviations, for α_e , turn out to be 3.75, 5.13 and 15.43 and for $\omega_e x_e$ 8.73, 17.23 and 27.49, respectively, against the respective values of 7.97 and 18.88 with Wei Hua's four-parameter potential. Also included are the values of dissociation energy determined with these potentials and these too corroborate the better performance of U_I and U_{II} . The relative worth of various potential functions has been further tested by carrying out numerical study of vibrational partition function (evaluated by sum over states method), entropy and thermal capacity for the ground state of 7 molecules and comparing these with the corresponding findings based on the RKR data.

Keywords. Four-parameter potential; dissociation energy; RKR curve; partition function.

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1. Introduction

In view of the importance of internuclear potential function in understanding the molecular structure, a good amount of effort has been devoted to their determination from energy level spectrum of diatomic molecules [1]. Most of these functions involve the use of three spectroscopic constants and are, thus, three-parameter potentials. A comparative study [2, 3] of their ability to represent potential energy curve and to predict the molecular constants reveals that though these broadly account for the overall shape of the curves, they lack credibility in depicting a correct picture of interaction, probably because they are based on

approximations which restrict the accuracy, particularly when the large amplitude vibrations of molecules are involved. For example, Steele *et al* [3], who compared 19 electronic states of diatomic molecules, concluded that although the average absolute deviation of the most commonly used Morse function from the RKR curve is 3.68%, the deviation is fairly large, close to the dissociation limit. The situation is no better with the empirical potential functions of Varshni [2] and Levine [4] which led to average deviations of 2.31% and 1.99%, respectively.

To overcome the problem of limited accuracy of the empirical internuclear potential function and also of the RKR method as it is confined to the region for which spectroscopic data exist, Dunham [5] expressed the potential function as a power series of the form

$$U(r) = a_0 \left(\frac{\Delta r}{r_e} \right)^2 \left[1 + a_1 \left(\frac{\Delta r}{r_e} \right) + a_2 \left(\frac{\Delta r}{r_e} \right)^2 + a_3 \left(\frac{\Delta r}{r_e} \right)^3 + \dots \right] + B_v J(J+1) \left[1 - 2 \frac{\Delta r}{r_e} + 3 \left(\frac{\Delta r}{r_e} \right)^2 - 4 \left(\frac{\Delta r}{r_e} \right)^3 + \dots \right] \quad (1)$$

and employed the second-order WKB approximation to get the eigenvalues as

$$G(v, J) = \sum_{i,j \geq 0} Y_{ij} (v + 1/2)^i [J(J+1)]^j. \quad (2)$$

Here, the coefficients Y_{ij} are explicitly related to the experimentally determined molecular constants. Furthermore, he showed that vibration-rotation interaction constant α_e and anharmonicity constant $\omega_e x_e$, are given by

$$\alpha_e = - \left[\frac{C_3}{C_2} r_e + 1 \right] \frac{6B_e^2}{\omega_e} \quad (3)$$

and

$$\omega_e x_e = B_e \left[\frac{15}{8} \left(\frac{C_3}{C_2} \right)^2 - \frac{3}{2} \frac{C_4}{C_2} \right] r_e^2, \quad (4)$$

where C_j are related to the derivatives of the potential function through

$$C_2 = \frac{U''(r_e)}{2!}, \quad C_3 = \frac{U'''(r_e)}{3!} \quad \text{and} \quad C_4 = \frac{U^{IV}(r_e)}{4!}. \quad (5)$$

Since the power series diverge for large r , the Dunham's approach may lead to a deviation of the potential curve near dissociation limit.

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

$$U_W(r) = D_e \left[\frac{1 - e^{-b(r-r_e)}}{1 - C e^{-b(r-r_e)}} \right]^2, \quad (6)$$

with $b = (1 - C)a$; and C an adjustable parameter having $|C| < 1$ and $a = \sqrt{k_e/2D_e}$. This potential was applied to 15 electronic states of diatomic molecules and has been found

to fit the RKR curves more closely as compared to Morse, Varshni and Levine potential functions even when the potential domain extends to near dissociation limit. Using U_W , we have deduced the molecular parameters α_e , $\omega_e x_e$ and the dissociation energies [7, 8] with the help of Dunham technique. While working on this problem we deliberated on three new FP potential functions and found that two of these display better agreement with the true RKR potential as compared to U_W which itself has been claimed to be superior to the Morse potential [6]. In order to assess the worth of the new potentials, we have considered the same 15 electronic states which Wei Hua used for his potential because of the availability of precisely known experimental molecular constants and of the accurately determined RKR potential curve up to near dissociation limit.

As a detailed application, which also provided a means for analysing the merit of the potential functions, we have calculated the vibrational partition function and therefrom entropy as well as thermal capacity of some diatomic molecules in their ground electronic state over wide range of temperatures. This part of investigation has also been motivated by the following considerations. First, the knowledge of partition function offers a doorway not only to obtaining the equilibrium thermodynamic quantities, and other related information, but also to developing microscopic models for various types of chemical reactions and activated rate processes [9–19]. Second, its zero-temperature limit has been used to evaluate the quantum-mechanical ground-state energy [20–24]. Third, in a number of chemical-physics problems involving gases one needs information about vibrational partition function at different temperatures [12, 25].

The exact value of partition function for a quantum-mechanical system (say, diatomic molecules) can be determined either by summation of the Boltzmann factors for various energy states [10, 11] or by finding the path-integral corresponding to the pertinent imaginary time action functional [10, 14, 15, 17, 18]. In addition, the variational perturbation method [25] and the thermal cluster cumulant (TCC) method [16, 19] can also be employed to evaluate the partition function and, like path integral technique, both of these do not involve prior knowledge of energy states. The sum over state approach involves knowledge of complete energy spectrum of the system, which proves to be a challenging task as one has to depend on either the precise spectroscopic data or the eigenvalues found by solving the Schrödinger equation for the well-guessed interaction potential. In addition to this inherent deficiency, in the case of vibrational partition functions, the procedure of direct summation has a limitation that it takes care of the contribution of the bound states while the contribution arising from the semibound and continuum states has to be accommodated separately [26, 27]. Of course, for the diatomic molecules the latter contribution is relevant only at temperatures large enough to significantly populate energy states with values, say, more than about 60–70% of the dissociation energy [25]. Nonetheless, the difficulty associated with the evaluation of all the bound state energies for diatomic molecules can be circumvented by the use of potential energy curves obtained by an appropriate method.

In the present work, the energy values for the bound states of the relevant potential function have been employed to determine the Boltzmann factors and hence various thermodynamic quantities. The calculations have been performed for such temperatures that the contribution of the semibound and continuum states can be ignored as pointed out above. Furthermore, since Wei Hua's potential can be solved to get exact eigenvalues for the vibrational states of interest, analytical expressions have been derived for the corresponding partition function and other thermodynamic properties. This has been done because such analytical results are better suited for the general discussion of temperature variation and

are useful in the analysis of some physico-chemical aspects such as isotope effects on the equilibrium constants [28]. For sake of completeness, we have also included our findings for some three-parameter potentials including the Morse potential, which has been subject of quite exhaustive study by many workers [25, 28–30].

2. New four-parameter potentials

The four-parameter potentials suggested by us are

$$U_{\text{I}}(r) = D_e \left[\frac{1 - \frac{r_e}{r} e^{-b_{\text{I}}(r^2 - r_e^2)}}{1 - K_{\text{I}} \frac{r_e}{r} e^{-b_{\text{I}}(r^2 - r_e^2)}} \right]^2, \quad (7)$$

$$U_{\text{II}}(r) = D_e \left[\frac{1 - \frac{r_e}{r} e^{-b_{\text{II}}(r^p - r_e^p)}}{1 - K_{\text{II}} \frac{r_e}{r} e^{-b_{\text{II}}(r^p - r_e^p)}} \right]^2, \quad (8)$$

and

$$U_{\text{III}}(r) = D_e \left[\frac{1 - e^{-x}}{1 - K_{\text{III}} e^{-x}} \right] \times \left[1 - A b x^{1/2} e^{-b(xr/r_e)^{1/2}} \right], \quad (9)$$

where

$$b_{\text{I}} = \frac{1}{2r_e^2} \left[\Delta^{1/2}(1 - K_{\text{I}}) - 1 \right], \quad (10)$$

$$b_{\text{II}} = \frac{1}{pr_e^p} \left[\Delta^{1/2}(1 - K_{\text{II}}) - 1 \right], \quad (11)$$

$$p = 2 + \left[\frac{1}{4}(\Delta^{1/2} - 4)(\Delta^{1/2} - 2)/(\Delta^{1/2} - 1) \right], \quad (12)$$

$$\Delta^{1/2} = ar_e, \quad (13)$$

$$x = \Delta(r - r_e)^2/(rr_e), \quad (14)$$

$$A = 0.8[1 - (1/b\Delta^{1/2})] \text{ and } b = 1.065. \quad (15)$$

Here, K_{I} , K_{II} and K_{III} are adjustable constants such that $|K_{\text{I}}|$, $|K_{\text{II}}|$ and $|K_{\text{III}}| < 1$. Following the same approach as for U_{W} , the adjustable constants K_{I} , K_{II} and K_{III} have been determined by the method of minimum deviation from the corresponding RKR potential curve whose values have been taken from the literature (references are given in table 1 which also includes the molecular constants used in these studies). Using the FP potentials alongwith the adjustable constants, mean square deviations ΔY defined by

$$\Delta Y_j = \frac{\sqrt{(U_j - U_{\text{RKR}})^2}}{D_e}, \quad (16)$$

where j stands for U_I , U_{II} , U_{III} potentials, have been derived for 15 molecular electronic states. The results and the respective constant values have been compiled in table 2. This

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	43
Na ₂ X ¹ Σ _g ⁺	3.0788	6022.600	159.177	0.873	0.1547	0.7254	11.4949	38
K ₂ X ¹ Σ _g ⁺	3.9244	4440.000	92.405	0.212	0.0562	0.3276	19.4800	46
Cl ₂ X ¹ Σ _g ⁺	1.9872	20276.440	559.751	1.516	0.2442	2.6943	17.4844	41
Cl ₂ B ³ Π	2.4311	3341.170	255.380	2.511	0.1631	4.8000	17.4844	37
I ₂ XO _g ⁺	2.6664	12547.335	214.520	0.113	0.0373 ₇	0.6079	63.4522	44, 45
IClX ¹ Σ ⁺	2.3209	17557.600	384.275	0.532	0.1142	1.4920	27.4147	36
IClA ³ Π ₁	2.6850	3814.700	211.030	0.744	0.0852 ₉	2.1200	27.4147	36, 40
IClA ³ Π ₂	2.6651	4875.520	224.571	0.674	0.0865	1.8823	27.4147	40
HFX 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	31
COX ¹ Σ ⁺	1.1283	90529.000	2169.813	17.504	1.9314	13.2883	6.8562	33, 34
XeOd ¹ Σ ⁺	2.8523	693.000	156.832	5.400	0.1456	9.8678	14.2327	35
Cs ₂ X ¹ Σ _g ⁺	4.6480	3649.500	42.020	0.022	0.0117	0.0826	66.4527	42
Rb ₂ X ¹ Σ _g ⁺	4.2099	3950.000	57.781	0.055	0.0224	0.1391	42.4559	39

Table 2. Mean square deviations (ref. eq. (16)) from the RKR curves for various potentials.

State	*C _W	k _I	k _{II}	k _{III}	ΔY _W (%)	ΔY _I (%)	ΔY _{II} (%)	ΔY _{III} (%)
Li ₂ X ¹ Σ _g ⁺	-0.1460	-0.0990	-0.1150	0.1040	2.842	0.570	0.846	2.735
Na ₂ X ¹ Σ _g ⁺	-0.2024	-0.1310	-0.1520	0.1950	2.028	0.273	0.314	3.025
K ₂ X ¹ Σ _g ⁺	-0.2780	-0.1680	-0.1908	0.2530	2.034	0.202	0.484	4.237
Cl ₂ X ¹ Σ _g ⁺	-0.1097	-0.0090	-0.0094	0.0040	3.502	1.969	1.975	1.851
Cl ₂ B ³ Π	-0.1036	-0.0100	0.0240	0.0260	2.258	3.313	3.623	3.153
I ₂ XO _g ⁺	-0.1460	-0.0469	-0.0244	0.0620	2.428	1.270	1.086	1.693
IClX ¹ Σ ⁺	-0.1000	0.0019	0.0088	-0.0159	3.298	1.825	1.743	1.409
IClA ³ Π ₁	-0.1680	-0.0759	-0.0339	0.1100	1.104	1.634	2.031	0.593
IClA ³ Π ₂	-0.1540	-0.0579	-0.0239	0.0860	1.260	1.384	1.605	0.718
HFX ¹ Σ ⁺	0.1120	0.0560	0.0545	-0.2589	3.093	0.501	0.538	3.342
H ₂ X ¹ Σ _g ⁺	0.1510	-0.0930	-0.0293	-0.2749	3.961	0.483	4.222	1.921
COX ¹ Σ ⁺	0.0370	0.0870	0.0658	-0.0810	0.548	0.834	0.600	3.523
XeOd ¹ Σ ⁺	-0.0940	0.0140	0.0135	0.0490	5.183	6.031	7.373	5.833
Cs ₂ X ¹ Σ _g ⁺	-0.2949	-0.1880	-0.2055	0.2970	1.889	0.389	0.409	4.699
Rb ₂ X ¹ Σ _g ⁺	-0.2890	-0.1750	-0.1963	0.2630	2.208	0.460	0.705	4.556
Average					2.670	1.450	1.860	2.890

* The values are slightly different from those obtained by Wei Hua [6], possibly because of reduced mass which we have taken from [47] for all the molecules.

Table 3. Deviations from the RKR energy values for various potentials.

J	U_{RKR}	$U_{\text{RKR}} - U_{\text{W}}$	$U_{\text{RKR}} - U_{\text{I}}$	$U_{\text{RKR}} - U_{\text{II}}$	$U_{\text{RKR}} - U_{\text{III}}$
$\text{Li}_2 X^1 \Sigma_g^+$					
40.00	8514.7770	130.8972	-0.1770	-17.7582	52.0796
30.00	7863.7080	100.0179	-1.0747	-14.3742	73.9966
20.00	6022.6580	60.6506	-31.0052	-34.9976	78.6502
10.00	3395.7980	18.1398	-32.7588	-30.8411	55.4056
0.00	175.0320	0.3807	-1.3071	-1.1843	0.6327
0.00	175.0320	0.4183	0.9608	0.7759	-1.2869
10.00	3395.7980	187.2985	-26.5788	-48.5903	-203.5434
20.00	6022.6580	468.2793	-103.9819	-153.1937	-449.2017
30.00	7863.7080	452.3038	-54.3991	-102.9306	-417.9621
40.00	8514.7770	-1.0426	2.0028	2.0019	-0.5434
Mean square deviation	ΔY	2.842	0.563	0.836	2.702
$\text{IClX}^1 \Sigma^+$					
73.00	17504.8400	375.4182	-212.8709	-206.4589	-15.6488
50.00	15032.5300	200.2333	-96.5539	-92.8997	121.3365
30.00	10232.9800	164.1870	-142.9163	-142.8911	49.7768
20.00	7222.4700	20.7485	-24.3526	-25.2397	117.9033
1.00	573.0300	-3.8916	2.2358	2.1297	6.0366
0.00	191.7700	1.0173	-1.3857	-1.4092	-0.7184
0.00	191.7700	1.7349	-1.2171	-1.1854	-1.5955
1.00	573.0600	6.5498	-3.5906	-3.4106	-4.7403
20.00	7222.4700	460.3147	-268.4762	-256.9364	-77.4287
40.00	12857.9200	1112.0520	-648.7313	-621.1204	-313.6082
50.00	15032.5300	1244.9470	-698.9514	-667.0984	-537.4015
73.00	17504.8400	16.9959	42.9428	44.2488	-40.5956
Mean square deviation	ΔY	3.297	1.825	1.743	1.409
$\text{I}_2 X O_g^+$					
108.00	12543.9300	-143.9722	-82.9008	-69.1417	18.4238
100.00	12506.1300	-141.7077	-81.3949	-67.7867	20.3799
75.00	11632.5600	-100.3151	-56.6763	-46.4106	53.9613
25.00	5050.0280	41.8271	24.2555	21.6334	105.8735
1.00	320.3986	2.6090	1.5562	1.3700	3.5038
0.00	107.0981	0.5716	0.3464	0.3066	0.7209
0.00	107.0981	-0.7577	-0.4755	-0.4240	-0.8099
1.00	320.3986	-4.0675	-2.5032	-2.2164	-4.0947
25.00	5050.0280	-346.1587	-213.4524	-187.8685	-222.9104
75.00	11632.5600	-381.3676	-29.5140	33.6656	-357.5953
100.00	12506.1300	27.7016	40.3433	40.7827	4.6363
108.00	12543.9300	3.3660	3.4004	3.4004	3.1521
Mean square deviation	ΔY	2.425	1.262	1.077	1.686

contd...

New four-parameter potentials

J	U_{RKR}	$U_{\text{RKR}} - U_{\text{W}}$	$U_{\text{RKR}} - U_{\text{I}}$	$U_{\text{RKR}} - U_{\text{II}}$	$U_{\text{RKR}} - U_{\text{III}}$
HFX¹Σ⁺					
19.00	49026.3800	1165.6610	-181.1774	-161.7322	-1173.3280
10.00	34362.5800	501.6085	-138.1061	-122.4648	-234.2140
1.00	6012.1800	18.4167	-46.5244	-44.3197	-12.2615
0.00	2050.7600	5.0204	-14.2955	-13.7842	-11.4038
0.00	2050.7600	5.4475	15.2745	14.5341	44.6006
1.00	6012.1800	61.8024	62.9374	58.8104	296.7749
10.00	34362.5800	2284.5700	-98.2256	-157.9720	3561.7380
19.00	49026.3800	1502.4880	-162.6737	-182.8747	-59.4633
Mean square deviation	ΔY	3.093	0.501	0.538	3.342
Cs₂X¹Σ_g⁺					
137.00	3629.0990	52.8580	-10.6621	-16.5119	39.8330
125.00	3560.1170	53.5146	-14.4752	-19.9042	36.2425
100.00	3215.5570	23.8178	2.3490	-1.3675	53.5540
50.00	1897.4550	-15.5051	11.3053	11.6669	54.2983
25.00	1016.5250	-11.8847	4.5392	5.4010	30.6510
1.00	62.8360	-0.3233	0.0371	0.0725	0.8245
0.00	20.9810	-0.0653	0.0057	0.0131	0.1692
0.00	20.9810	0.0816	-0.0102	-0.0191	-0.2053
1.00	62.8360	0.4289	-0.0378	-0.0868	-10.1069
25.00	1016.5250	36.9406	-3.5752	-7.8745	-91.8515
50.00	1897.4550	98.3256	-10.0920	-21.5495	-232.5739
100.00	3215.5570	128.1972	19.2324	1.2129	-331.1103
125.00	3560.1170	37.0991	38.2099	30.9517	-168.1275
137.00	3629.0990	-3.755	17.9210	16.9826	-57.2426
Mean square deviation	ΔY	1.899	0.389	0.410	4.699

table also contains, for comparison, the corresponding values obtained from U_{W} which, as stated earlier, itself fits the RKR curve more closely as compared to three-parameter potentials [6]. The respective percentage average mean square deviations for U_{W} , U_{I} , U_{II} and U_{III} are 2.67, 1.45, 1.86 and 2.89. It may be noted that eq. (12), is the same as introduced by Levine [4]. Furthermore, in order to check the efficacy of the new potentials near dissociation limit we have compared their performance for 5 electronic states in table 3.

3. Evaluation of spectroscopic constants α_e and $\omega_e x_e$

Dunham [5], on the basis of wave mechanics, showed that molecular parameters can be derived fairly accurately from the eqs (3) and (4) if the potential function can be expressed as in eq. (1). Employing his method, we have derived the following expressions for molecular parameters corresponding to different potentials.

$$(\alpha_e)_I = F \left[\Delta(1 + K_I) + \frac{2}{\Delta^{1/2}(1 - K_I)} - 2 \right], \quad (17)$$

$$(\omega_e x_e)_I = B_e \left[\frac{6K_I}{(1-K_I)} - \frac{3}{2} K_I \Delta^{1/2} (1+K_I) + \frac{6}{\Delta(1-K_I)^2} + 3K_I \Delta + \frac{9}{2} + \Delta(1-K_I)^2 - \frac{7}{\Delta^{1/2}(1-K_I)} \right], \quad (18)$$

$$(\alpha_e)_{II} = F \left[\Delta(1+K_{II}) + \frac{p}{\Delta^{1/2}(1-K_{II})} - p \right], \quad (19)$$

$$(\omega_e x_e)_{II} = B_e \left[\frac{6K_{II}}{(1-K_{II})} - \frac{3}{4} p K_{II} \Delta^{1/2} + 3K_{II} \Delta + \left(\frac{15}{8} p^2 - \frac{3}{2} \right) \frac{1}{\Delta(1-K_{II})^2} + \frac{15}{8} p^2 - 3 + \Delta(1-K_{II})^2 + \left(\frac{1}{2} - \frac{15}{4} p(p-1) \right) \frac{1}{\Delta^{1/2}(1-K_{II})} + \left(6 - \frac{15}{4} p \right) \Delta^{1/2} \right], \quad (20)$$

$$(\alpha_e)_{III} = F \left(\frac{4}{5} \right) [1.065 \Delta^{1/2} (1-K_{III})^{1/2} - 1], \quad (21)$$

and

$$(\omega_e x_e)_{III} = (B_e/8) [3 + 6\Delta(1-K_{III}) + 12\Delta K_{III}]. \quad (22)$$

Here,

$$F = \left[6B_e^2 / \omega_e \Delta^{1/2} \right]. \quad (23)$$

The values of α_e and $\omega_e x_e$, calculated from these relations have been projected in tables 4 and 5, respectively. Average mean deviations from the experimental values for α_e are 3.75, 5.13 and 15.43, respectively, and are 8.73, 17.23 and 27.49, respectively, for $\omega_e x_e$. The relevant magnitudes pertaining to U_W are 7.97 and 18.88. The results for U_I and U_{II} are certainly more encouraging than those for U_W [7] which itself yields values better than the three-parameter potentials of Morse, Varshni and of Levine [7].

4. Estimation of the dissociation energy

As a further test of the reliability of the new potentials and as an application, the dissociation energy has also been computed for molecules considered here. This aim has been achieved by iteration method, explained in [8]. As mentioned therein, starting from the approximate values of D_e obtained from linear extrapolation, $D_e = \omega_e^2 / 4\omega_e x_e$ and of adjustable constants found using the fact that it is always less than unity, the relevant potential energy curves have been calculated. The process is repeated several times with periodically changed values of D_e and adjustable constants. The process is continued till ΔY_j is minimum. The value of D_e that corresponds to minimum deviation ΔY_j in the final scan

Table 4. Comparison of experimental values of α_e with calculated values and the mean deviations $[\Delta X_j = (\alpha_e(\text{exptl}) - \alpha_e(j)) / (\alpha_e(\text{exptl}))]$; where $\alpha_e(j)$ stands for, $\alpha_e(\text{W})$, $\alpha_e(\text{I})$, $\alpha_e(\text{II})$, $\alpha_e(\text{III})$, for the corresponding electronic states given in table 1.

$\alpha_e(\text{exptl})$ (10^3 cm^{-1})	$\alpha_e(\text{W})$ (10^3 cm^{-1})	$\alpha_e(\text{I})$ (10^3 cm^{-1})	$\alpha_e(\text{II})$ (10^3 cm^{-1})	$\alpha_e(\text{III})$ (10^3 cm^{-1})	ΔX_{W} (%)	ΔX_{I} (%)	ΔX_{II} (%)	ΔX_{III} (%)
7.040	7.588	6.762	6.872	8.281	7.79	3.94	2.38	17.63
0.873	0.974	0.851	0.870	1.076	11.54	2.46	0.34	23.27
0.212	0.228	0.209	0.212	0.278	7.55	1.43	0.06	30.97
1.516	1.624	1.559	1.560	1.650	7.15	2.88	2.93	8.87
2.511	2.439	2.360	2.339	2.439	2.87	6.01	6.83	5.45
0.113	0.126	0.121	0.120	0.128	11.65	7.36	6.59	13.62
0.532	0.583	0.563	0.562	0.588	9.55	5.89	5.66	10.44
0.744	0.799	0.770	0.760	0.807	7.48	3.49	2.17	8.45
0.674	0.724	0.698	0.691	0.730	7.47	3.65	2.58	8.30
772.400	803.299	757.318	759.243	728.560	4.00	1.95	1.70	5.68
3051.300	3328.243	2911.486	2440.850	2962.687	9.08	4.58	20.01	2.90
17.504	17.436	17.168	17.197	15.453	0.39	1.92	1.75	11.71
5.400	4.925	5.009	4.432	4.611	8.79	7.25	17.92	14.60
0.022	0.024 ₇	0.022 ₁	0.022 ₄	0.029	12.19	0.44	1.90	32.61
0.055	0.061 ₇	0.056 ₇	0.057 ₃	0.075 ₃	12.11	3.04	4.20	36.99
Average					7.97	3.75	5.13	15.43

Table 5. Comparison of experimental values of $\omega_e x_e$ with calculated values and the mean deviations $[\Delta X_j = (\omega_e x_e(\text{exptl}) - \omega_e x_e(j)) / \omega_e x_e(\text{exptl})]$; where $\omega_e x_e(j)$ stands for $\omega_e x_e(\text{W})$, $\omega_e x_e(\text{I})$, $\omega_e x_e(\text{II})$, $\omega_e x_e(\text{III})$, for the corresponding electronic states given in table 1.

$\omega_e x_e(\text{exptl})$ cm^{-1}	$\omega_e x_e(\text{W})$ cm^{-1}	$\omega_e x_e(\text{I})$ cm^{-1}	$\omega_e x_e(\text{II})$ cm^{-1}	$\omega_e x_e(\text{III})$ cm^{-1}	ΔX_{W} (%)	ΔX_{I} (%)	ΔX_{II} (%)	ΔX_{III} (%)
2.6100	3.1728	2.6288	2.8873	3.2534	21.56	0.72	10.63	24.65
0.7254	0.8184	0.7342	0.8248	1.0004	21.57	1.22	13.70	37.91
0.3276	0.3842	0.3266	0.3636	0.4729	17.28	0.31	11.00	44.35
2.6943	3.4853	3.1358	3.1433	3.0006	29.36	16.39	16.67	11.37
4.8000	4.4261	4.0550	3.5255	3.8150	7.79	15.52	26.55	20.52
0.6079	0.8025	0.7272	0.6599	0.7443	32.01	19.62	8.56	22.43
1.4920	1.9131	1.7365	1.6876	1.5949	22.22	16.39	13.11	6.90
2.1210	2.5102	2.2875	1.9010	2.4611	18.41	7.90	10.33	16.09
1.8823	2.2487	2.0461	1.7661	2.1366	19.47	8.70	6.17	13.51
89.8800	97.4800	83.7665	84.8220	56.0408	8.46	6.80	5.63	37.65
120.6020	148.4096	115.9353	39.1383	91.5887	23.06	3.87	67.55	24.06
13.2883	13.4985	12.2123	13.2296	9.6844	1.58	8.10	0.44	27.12
9.8678	8.1163	7.8198	5.2033	7.0352	17.75	20.75	47.28	28.71
0.0826	0.0958	0.0813	0.0886	0.1216	15.97	1.62	7.30	47.22
0.1391	0.1679	0.1433	0.1578	0.2085	20.68	2.99	13.50	49.89
Average					18.88	8.73	17.23	27.49

is regarded as the best estimate of D_e . It may be pointed out that, since the vibrational spacings [48], rotational constants [49] and other properties [50] of the diatomic molecules in highly excited vibrational states are explained by the outer turning points, adjustable constant pertaining to right limb of the potential curve have been used for the calculations

Table 6. Comparison of experimental values of D_e with calculated values and the mean deviations $\Delta X = (D_e(\text{exptl}) - D_e(j))/D_e(\text{exptl})$; where $D_e(j)$ stands for, $D_e(\text{I})$, $D_e(\text{II})$, $D_e(\text{III})$; for the fifteen electronic states.

$D_e(\text{exptl})$ (cm^{-1})	K_{I} $r > r_e$	K_{II} $r > r_e$	K_{III} $r > r_e$	$D_e(\text{I})$ (cm^{-1})	$D_e(\text{II})$ (cm^{-1})	$D_e(\text{III})$ (cm^{-1})	ΔX_{I} (%)	ΔX_{II} (%)	ΔX_{III} (%)	E_{max} D_e
*8516.78	-0.132	-0.164	-0.281	8502	8515	8557	0.17	0.02	0.47	0.9998
*6022.00	-0.143	-0.197	-0.341	5996	5998	6037	0.44	0.41	0.24	0.9961
**4440.00	-0.181	-0.212	-0.466	4436	4468	4301	0.09	0.63	3.13	0.8306
*20276.40	-0.129	-0.131	-0.157	20383	20380	20644	0.52	0.51	1.18	0.9995
*3341.17	+0.180	+0.233	+0.429	3269	3265	3327	2.17	2.27	0.42	0.9990
*12547.00	-0.160	-0.118	-0.169	12422	12409	12576	0.99	1.10	0.23	0.9997
**17557.00	-0.111	-0.100	-0.084	17621	17607	17958	0.36	0.28	2.28	0.9970
+3814.00	-0.068	-0.033	+0.048	3699	3671	3765	3.03	3.77	1.30	0.9934
**4875.00	-0.100	-0.030	-0.008	4711	4708	4813	3.37	3.43	1.28	0.9853
++49384.00	+0.610	+0.060	+0.291	50048	50097	50092	1.34	1.44	3.25	0.9928
+38297.00	-0.088	+0.059	+0.082	38391	37335	39259	0.24	2.51	2.51	0.9922
+90529.00	+0.120	+0.101	+0.179	89846	91174	82650	0.75	0.71	8.70	0.6995
**693.00	+0.091	+0.406	+0.632	642	648	686	7.30	6.49	1.01	0.9476
*3649.50	-0.208	-0.200	-0.366	3607	3647	3653	1.16	0.06	0.10	0.9944
**3950.00	-0.193	-0.225	-0.507	3966	3993	3818	0.40	1.08	3.45	0.8388
Average							1.48	1.63	2.01	

$D_e(\text{exptl.})$ values are derived from NDE long range technique (*), RKR potential curve (**), extrapolation from the RKR curve (+), and limiting curve of dissociation (++)

of D_e as elaborated in [8]. The values so found and the respective dissociation energies obtained with U_{I} , U_{II} and U_{III} have been displayed in table 6.

5. Appraisal of the potential functions

A good potential, in the first place, must satisfy the following necessary criteria,

$$U(r_e) = U'(r_e) = 0, \quad (24)$$

$$U(\infty) = D_e, \quad (25)$$

$$U''(r_e) = 2D_e a^2 = k_e = \mu \omega_e^2. \quad (26)$$

Moreover, it is expected that $U(0) = \infty$. This is, however, not a strict condition, because results are practically the same if U becomes very large at $r = 0$ and, furthermore, the curve close to $r = 0$ does not have practical significance. In addition to the above, the suitability of a potential function is checked in two ways: first and foremost, by comparing it with the experimental curve (the RKR potential curve in our case) and secondly, by seeing how accurately the molecular parameters, not used in the potential, can be derived. Like U_{W} and the three-parameter potentials, U_{I} , U_{II} and U_{III} also satisfy the criteria enunciated in eqs (24)–(26). Their ability to represent true RKR potential curves has been demonstrated in tables 2 and 3. Except for the molecular states $\text{IClA}^3\Pi_1$, $\text{IClA}^3\Pi_2$, $\text{COX}^1\Sigma^+$ and $\text{XeOd}^1\Sigma^+$, U_{I} and U_{II} potential curves match the RKR curves more closely. Even for the states listed above, the deviation is only marginally higher ($< 0.8\%$) than the U_{W} . The reliability of these potentials close to dissociation limit has been displayed for arbitrarily chosen 5 molecular states in table 3. These exhibit very clearly the accuracy of U_{I} , U_{II} and U_{III} in comparison with U_{W} and hence the better known three-parameter potentials.

It may be mentioned that U_W leads to solvable Schrödinger equation, exactly for zero angular momentum and approximately for non-zero angular momentum [6], while the wave equation corresponding to U_I , U_{II} and U_{III} is not amenable to analytical solution. This situation is parallel to that prevailing in three-parameter potential functions, where Schrödinger equation admits analytical solution for Morse potential but not for the potential functions of Varshni, Levine and Lippincott. In spite of this, the last three potentials occupy a prestigious position because the comparative studies [2–4] have established that these potentials, though relatively slightly complex, lead to better results in fitting the experimental potential energy curve and in predicting the molecular constants in comparison with the Morse potential. Similarly, the potentials

$$V(r) = D_e - \sum_n \frac{C_n}{r^n}, \quad (27)$$

which include the long range forces and have led to the development of WKB based NDE technique [51] for the prediction of D_e , do not lead to solvable wave equation, yet provides close fit to RKR curve and predicts dissociation energy more precisely. That is, as far as molecular structure is concerned, one may forgo the solvability of the Schrödinger equation. Consequently, for the study of molecular structure U_I and U_{II} are more accurate than U_W and the better known three-parameter potentials including the Morse potential. However, U_{III} is just comparable to U_W .

This conclusion is further substantiated by the evaluation of molecular constants, α_e and $\omega_e x_e$ with these potentials (tables 4 and 5). The values of α_e found through U_I are much closer to the experimental values as compared to U_W except for $\text{Cl}_2 B^3\Pi_u$ and $\text{COX}^1\Sigma_g^+$ for which U_W yields better results. Similar remarks hold good for U_{II} potential which basically differs from U_I in the exponent of r ; 2 in case of U_I for all molecules and p for U_{II} , whose value is given by eq. (12) and is mostly close to 2 for all molecules except H_2 [4]. The anomaly in p for H_2 is reflected in large deviation in the value of α_e with U_{II} . However, if p is taken, like for all other molecules, around 2, the deviation turns out to be less than U_W potential. The above situation also prevails for the anharmonicity constant $\omega_e x_e$ (table 5).

Table 7. Comparison of least square fitted values of ω_e and $\omega_e x_e$ of RKR curve with the respective values of ω_e and $\omega_e x_e$ for all FP potentials for the corresponding electronic states given in table 1.

ω_e (RKR) cm^{-1}	ω_e (W) cm^{-1}	ω_e (I) cm^{-1}	ω_e (II) cm^{-1}	ω_e (III) cm^{-1}	$\omega_e x_e$ (RKR) cm^{-1}	$\omega_e x_e$ (W) cm^{-1}	$\omega_e x_e$ (I) cm^{-1}	$\omega_e x_e$ (II) cm^{-1}	$\omega_e x_e$ (III) cm^{-1}
358.178	350.022	353.386	354.589	320.981	3.2973	3.3558	3.3124	3.3124	2.5849
181.662	168.759	180.539	178.647	150.425	1.1485	1.3585	1.3348	1.3051	0.9257
92.904	92.264	92.726	92.648	69.597	0.4273	0.3809	0.3833	0.3911	0.1229
570.643	555.118	560.118	560.096	566.838	3.4947	3.5570	3.5242	3.5237	3.6064
255.668	259.136	262.264	262.065	259.761	4.9846	4.9534	5.0650	5.1996	5.0701
220.409	215.159	217.588	218.045	208.225	0.8892	0.9072	0.8880	0.8892	0.8095
390.995	381.439	384.814	384.784	397.386	1.9583	1.9232	1.9201	1.9576	2.0673
216.146	213.901	216.366	217.276	197.409	2.9584	3.0434	2.9683	2.9806	2.4948
229.973	226.325	228.651	229.351	213.504	2.5429	2.6415	2.5314	2.5344	2.2108
4126.595	4074.016	4132.076	4130.740	5161.985	85.1838	81.4570	82.7891	82.7904	133.3643
4404.484	4299.507	4411.104	4587.833	5487.498	121.6698	118.7263	119.1424	121.0672	195.7831
2166.835	2166.115	2174.366	2172.914	2362.840	13.3700	12.8221	11.9183	12.2001	15.2823
133.194	159.395	160.483	161.169	155.079	9.1263	5.9333	9.1017	9.6179	9.1425
42.853	42.264	42.841	42.768	30.461	0.1141	0.1109	0.1101	0.1103	0.0361
58.140	57.797	58.112	58.065	43.090	0.1923	0.1651	0.1711	0.1743	0.0516

The improved accuracy and consistency of the newly proposed FP potentials are also supported by the values of ω_e and $\omega_e x_e$ obtained by their linear scale fitting (table 7). To facilitate the comparison, we have also included in this table the corresponding results for the RKR potential curve.

A perusal of table 6 shows that U_I and U_{II} predict the dissociation energy generally, within a proximity of 1% of the experimental values. The variation depends upon the technique applied to obtain the experimental value. For example, in XeO levels up to $v = 8$ have been observed experimentally yielding $E_{\max}/D_e = 0.9476$. Therefore, one cannot rule out the possibility of error in experimental values. In the case of ICl the reported vibrational perturbations near the dissociation and the merging approach employed to obtain D_e values [9, 36, 40, 52] may account for relatively large deviations. The overall performance of U_I , U_{II} , U_{III} with average mean deviations of 1.48%, 1.63% and 2.01% is found to be better than that of U_W which has the corresponding value 2.7% [8].

6. Vibrational partition function, entropy and thermal capacity

The contribution of the bound states to the vibrational partition function of a diatomic molecule at temperature T can be written as

$$Q = \sum_{n=0}^N \exp(-\beta E_n), \quad (28)$$

where $\beta = (k_B T)^{-1}$ with k_B as Boltzmann constant and E_n is the energy of the n th bound state. The E_n values can be obtained (i) from the spectroscopic data, (ii) as eigenvalues when the Schrödinger equation for the potential energy function is analytically or numerically solved, (iii) using some method for extracting their values from the potential energy curves. It is conventional to take $E_n = 0$ corresponding to the minimum of the potential. The entropy and thermal capacity are, respectively, related to Q through

$$S = k_B [\ln Q - (\beta/Q)(\partial Q/\partial\beta)] \quad (29)$$

and

$$C = k_B \beta^2 [Q^{-1}(\partial^2 Q/\partial\beta^2) - Q^{-2}(\partial Q/\partial\beta)^2]. \quad (30)$$

Using eq. (28), the first and second derivatives of Q appearing above can be expressed as

$$\partial Q/\partial\beta = - \sum_n E_n \exp(-\beta E_n) \quad (31)$$

and

$$\partial^2 Q/\partial\beta^2 = \sum_n E_n^2 \exp(-\beta E_n). \quad (32)$$

New four-parameter potentials

Table 8. A comparison of vibrational partition functions, entropy ($\text{JK}^{-1} \text{mol}^{-1}$) and thermal capacity ($\text{JK}^{-1} \text{mol}^{-1}$) found by various methods (see text for meaning of symbols employed) at different temperatures for (a) H_2 , (b) Li_2 , (c) HF , (d) CO , (e) Cl_2 , (f) ICl , (g) I_2 molecules.

Temp	j	RKR	ME	M	V	Le	Li	WE	W	WI	WII	I	II	III
8(a)														
500	3	1.888	1.947	1.796	2.476	1.862	1.740	1.949	2.203	1.949	1.949	1.951	1.688	1.863
1000	2	4.356	4.423	4.247	4.994	4.323	4.179	4.426	4.709	4.426	4.426	4.428	4.115	4.324
2000	1	2.195	2.214	2.162	2.376	2.173	2.139	2.217	2.299	2.214	2.214	2.210	2.111	2.173
3000	1	4.081	4.108	4.026	4.369	4.011	3.980	4.119	4.254	4.108	4.108	4.090	3.910	4.012
500	4	6.828	7.023	5.467	13.452	4.142	4.459	7.536	10.507	3.816	7.235	6.026	2.955	4.215
1000	1	1.465	1.488	1.321	2.012	1.168	1.206	1.542	1.803	1.146	1.526	1.387	0.992	1.164
2000	0	1.768	1.784	1.692	2.063	1.578	1.616	1.817	1.967	1.602	1.805	1.723	1.460	1.577
3000	0	3.948	3.980	3.861	4.406	3.618	3.724	4.039	4.292	3.717	3.999	3.879	3.431	3.625
500	3	7.478	7.749	6.114	13.875	4.910	5.166	8.377	11.289	10.263	17.718	6.784	3.530	4.732
1000	1	7.546	7.642	6.962	9.660	6.309	6.477	7.858	8.882	9.661	13.398	7.229	5.536	6.289
2000	0	4.262	4.291	4.183	4.675	3.949	4.052	4.347	4.580	4.855	5.912	4.197	3.768	3.955
3000	0	6.402	6.457	6.443	6.788	6.022	6.271	6.534	6.811	6.863	7.918	6.353	5.862	6.063
8(b)														
50	3	6.495	6.537	7.249	6.916	7.040	6.891	6.537	6.573	6.539	6.539	6.318	6.351	6.740
200	1	3.096	3.106	3.226	3.170	3.190	3.165	3.108	3.117	3.107	3.108	3.073	3.079	3.144
400	1	7.505	7.544	7.872	7.715	7.768	7.693	7.559	7.597	7.552	7.555	7.470	7.487	7.658
600	0	1.174	1.184	1.245	1.214	1.224	1.209	1.187	1.195	1.185	1.185	1.171	1.173	1.205
50	3	4.291	4.528	6.900	5.725	6.107	5.580	4.637	4.934	3.826	4.616	4.169	4.260	5.336
200	1	2.604	2.640	2.917	2.787	2.830	2.768	2.656	2.696	2.568	2.654	2.589	2.603	2.744
400	0	7.101	7.186	7.668	7.426	7.503	7.381	7.221	7.295	7.134	7.205	7.090	7.117	7.367
600	0	10.296	10.430	11.038	10.712	10.810	10.641	10.486	10.580	10.510	10.440	10.300	10.337	10.654
50	2	3.892	5.893	5.893	5.003	5.300	4.893	4.159	4.388	4.822	5.921	3.786	3.867	4.705
200	0	5.133	5.184	5.489	5.339	5.388	5.312	5.205	5.252	5.397	5.549	5.123	5.140	5.300
400	0	7.513	7.608	7.907	7.724	7.774	7.672	7.647	7.698	7.572	3.216	7.534	7.557	7.717
600	0	8.194	8.350	8.671	8.435	8.491	8.358	8.411	8.463	7.801	-0.392	8.249	8.276	8.453
8(c)														
200	7	3.914	4.008	2.967	2.747	2.783	2.426	4.015	4.071	4.017	4.017	3.507	3.526	2.840
1000	2	5.248	5.273	4.963	4.886	4.898	4.764	5.275	5.291	5.275	5.276	5.133	5.138	4.917
2000	1	2.429	2.434	2.352	2.327	2.330	2.291	2.437	2.445	2.435	2.436	2.397	2.399	2.327
4000	1	6.340	6.346	6.183	6.098	6.107	6.007	6.367	6.412	6.348	6.357	6.269	6.273	6.034
200	3	1.150	1.140	0.878	0.728	0.738	0.598	1.207	1.341	0.755	1.180	1.017	1.028	0.594
1000	1	1.902	1.865	1.646	1.508	1.522	1.377	1.912	2.008	1.565	1.902	1.766	1.773	1.370
2000	0	1.975	1.972	1.862	1.780	1.788	1.703	1.998	2.050	1.836	1.991	1.921	1.925	1.689
4000	0	6.258	6.258	6.095	5.897	5.913	5.741	6.322	6.450	6.076	6.270	6.163	6.172	5.632
200	2	1.214	1.204	0.937	0.795	0.812	0.668	1.257	1.380	1.569	1.359	1.079	1.089	0.662
1000	1	9.128	9.098	8.263	7.714	7.769	7.181	9.275	9.638	1.093	1.397	8.722	8.751	7.148
2000	0	4.509	4.506	4.371	4.240	4.252	4.125	4.547	4.628	4.933	5.699	4.436	4.442	4.072
4000	0	7.546	7.568	7.573	7.350	7.362	7.238	7.643	7.794	7.605	8.320	7.514	7.521	6.999
8(d)														
200	4	4.170	4.173	4.003	3.698	3.799	3.741	4.175	4.127	4.175	4.175	4.070	4.078	3.824
1000	1	2.210	2.210	2.190	2.148	2.162	2.154	2.211	2.206	2.211	2.211	2.198	2.199	2.164
3000	1	9.306	9.304	9.212	9.043	9.104	9.056	9.317	9.301	9.312	9.314	9.254	9.261	9.086
5000	0	1.609	1.609	1.595	1.553	1.566	1.612	1.609	1.610	1.611	1.611	1.597	1.599	1.558
200	5	2.725	2.569	2.598	1.298	1.734	1.207	2.903	2.177	2.237	3.143	2.830	2.431	2.076
1000	0	1.625	1.624	1.592	1.503	1.532	1.510	1.630	1.624	1.590	1.620	1.603	1.606	1.525
3000	0	8.552	8.548	8.476	8.232	8.308	8.234	8.572	8.557	8.552	8.564	8.486	8.497	8.252
5000	0	12.714	12.709	12.626	12.291	12.392	12.274	12.752	12.731	12.928	12.723	12.616	12.634	12.274
200	4	4.243	4.138	3.870	3.050	3.375	3.445	3.865	4.348	5.246	5.670	3.493	3.909	2.450
1000	0	3.998	3.998	3.950	3.811	3.856	3.820	4.007	3.998	4.126	4.332	3.964	3.969	3.840
3000	0	7.819	7.815	7.789	7.633	7.677	7.610	7.841	7.831	7.704	7.938	7.767	7.777	7.590
5000	0	8.429	8.426	8.412	8.204	8.259	8.151	8.472	8.460	7.686	7.734	8.352	8.369	8.097

contd...

Table 8. Contd...

Temp	j	RKR	ME	M	V	Le	Li	WE	W	WI	WII	I	II	III
8(e)														
100	2	1.670	1.808	1.815	1.710	1.710	1.725	1.809	1.817	1.809	1.809	1.702	1.702	1.753
500	1	5.526	5.640	5.726	5.578	5.578	5.592	5.645	5.730	5.644	5.645	5.567	5.567	5.620
1000	0	1.211	1.231	1.267	1.226	1.226	1.227	1.234	1.268	1.235	1.233	1.223	1.223	1.231
1500	0	1.860	1.892	1.968	1.890	1.890	1.888	1.898	1.970	1.894	1.895	1.885	1.885	1.891
100	2	2.454	2.643	3.251	2.628	2.631	2.673	2.674	3.270	2.426	2.672	2.586	2.587	2.768
500	0	5.259	5.339	5.605	5.347	5.348	5.354	5.357	5.613	5.292	5.353	5.328	5.329	5.380
1000	0	10.512	10.640	11.072	10.672	10.674	10.648	10.678	11.083	10.726	10.657	10.645	10.646	10.648
1500	0	13.883	14.062	14.614	14.111	14.114	14.045	14.120	14.628	14.458	14.064	14.079	14.080	14.006
100	1	1.752	1.865	2.219	1.856	1.858	1.883	1.883	2.231	2.064	2.332	1.831	1.832	1.939
500	0	6.834	6.889	7.103	6.914	6.915	6.896	6.909	7.108	6.965	7.199	6.901	6.902	6.887
1000	0	8.116	8.210	8.483	8.253	8.254	8.174	8.250	8.488	7.814	8.213	8.240	8.240	8.104
1500	0	8.496	8.659	8.980	8.700	8.701	8.568	8.724	8.986	7.350	8.033	8.686	8.687	8.445
8(f)														
50	3	4.012	4.030	4.453	4.150	4.129	4.189	4.031	4.217	4.031	4.031	4.155	4.151	4.200
500	1	8.664	8.691	8.970	8.744	8.728	8.755	8.701	8.802	8.698	8.699	8.748	8.745	8.761
1000	0	1.813	3.295	5.174	5.103	5.105	5.063	3.304	5.064	3.299	3.300	5.074	5.118	5.084
1500	0	2.760	2.787	2.928	2.806	2.798	2.796	2.798	2.843	2.788	2.790	2.808	2.806	2.796
50	3	1.709	1.766	2.365	1.814	1.777	1.841	1.794	1.938	1.601	1.786	1.822	1.812	1.854
500	1	8.010	8.059	8.406	8.117	8.096	8.111	8.080	8.198	8.054	8.074	8.121	8.117	8.115
1000	0	13.596	13.703	14.196	13.769	13.739	13.716	13.747	13.906	14.003	13.716	13.775	13.768	13.716
1500	0	17.055	17.223	17.816	17.283	17.243	17.176	17.291	17.471	18.121	17.210	17.290	17.279	17.167
50	2	1.720	1.769	2.291	1.811	1.779	1.841	1.787	1.926	1.976	2.249	1.818	1.779	1.854
500	0	7.644	7.697	7.903	7.731	7.720	7.694	7.719	7.792	7.631	7.841	7.734	7.730	7.691
1000	0	8.380	8.497	8.725	8.490	8.475	8.383	8.544	8.595	7.563	7.940	8.493	8.487	8.371
1500	0	8.675	8.877	9.139	8.850	8.831	8.688	8.955	9.003	6.277	5.212	8.853	8.845	8.667
8(g)														
50	2	4.597	4.606	4.889	4.726	4.688	4.735	4.604	4.698	4.607	4.607	4.661	4.654	4.706
200	1	5.904	5.916	6.117	5.998	5.970	5.999	5.918	5.981	5.987	5.919	5.952	5.946	5.982
400	0	1.278	1.279	1.334	1.301	1.293	1.299	1.281	1.297	1.280	1.281	1.288	1.287	1.296
1000	0	3.326	3.325	3.541	3.404	3.373	3.381	3.338	3.398	3.328	3.329	3.356	3.349	3.378
50	1	1.284	1.304	1.593	1.416	1.377	1.416	1.311	1.393	1.256	1.311	1.350	1.342	1.393
200	0	5.552	5.578	5.907	5.708	5.662	5.699	5.589	5.686	5.551	5.588	5.632	5.622	5.679
400	0	10.900	10.865	11.357	11.054	10.984	11.018	10.889	11.031	10.938	10.880	10.941	10.925	11.001
1000	0	18.558	18.641	19.397	18.901	18.788	18.759	18.704	18.907	19.752	18.633	18.733	18.700	18.784
50	1	6.794	6.877	8.047	7.340	7.178	7.337	6.908	7.245	7.233	7.709	7.070	7.037	7.246
200	0	6.946	6.944	7.169	7.029	6.997	7.007	6.957	7.021	6.987	7.132	6.978	6.970	7.003
400	0	8.245	8.116	8.369	8.201	8.163	8.139	8.140	8.209	7.847	8.107	8.146	8.135	8.157
1000	0	8.466	8.846	9.151	8.893	8.837	8.717	8.916	8.963	5.823	3.943	8.828	8.803	8.796

7. Analytical expressions for Q corresponding to U_W

In order to find an analytical expression for the vibrational partition function pertaining to U_W , we have adopted the formalism recommended by Fernandez and Castro [30]. As mentioned earlier, Wei Hua [6] obtained eigenvalue for U_W , which can be written in the Dunham form as

$$E_n(U_W) \simeq A_0 + A_1 \left(n + \frac{1}{2} \right) + A_2 \left(n + \frac{1}{2} \right)^2, \tag{33}$$

where

$$A_0 = (\omega_e^2/4D_e) \left[\frac{C}{4} - \left[\frac{C\omega_e(1+C)}{16D_e} \right]^2 \right], \tag{34}$$

New four-parameter potentials

$$A_1 = \omega_e \left[1 - \frac{C(1+C+C^2)\omega_e^2}{32D_e^2} \right] \quad (35)$$

and

$$A_2 = (\omega_e^2/4D_e) \left[-1 - C - C^2 + \frac{3}{8} \left[\frac{C\omega_e(1+C)}{D_e} \right]^2 \right]. \quad (36)$$

Here, we have retained terms up to second degree in $(n + \frac{1}{2})$ and have also omitted terms higher than $[\omega_e(1-C)/2D_e]^2$.

In this case the vibrational partition function is given by

$$Q_W = G(\beta, \omega_e, D_e, C) \sum_{n=0}^N e^{-\beta[nA_1 + n(n+1)A_2]} \quad (37)$$

with

$$G(\beta, \omega_e, D_e, C) = e^{-(\beta/4)(4A_0 + 2A_1 + A_2)}. \quad (38)$$

Proceeding as in [30] we have expanded the second factor in the exponential in eq. (37) in power series in A_2/A_1 in two different ways and by terminating the series at A_2/A_1 itself, for computational convenience, we arrived at the following two expressions for the partition function,

$$Q_W^{(1)} = G[g^{(1)}(\beta, \omega_e, D_e, C)(1 - 2\beta A_2 \lambda(1 - \lambda)^{-2} + (N + 1)\beta A_2 \lambda^{N+1}(1 - \lambda)^{-1}\{N + 2(1 - \lambda)^{-1}\}] \quad (39)$$

and

$$Q_W^{(2)} = G[g^{(2)}(\beta, \omega_e, D_e, C)(1 - \beta A_2 \zeta(1 + \zeta)(1 - \zeta)^{-2} + (N + 1)\beta A_2 \zeta^{N+1}(1 - \zeta)^{-1}\{N + (1 + \zeta)(1 - \zeta)^{-1}\}]. \quad (40)$$

The symbols used here have following meaning,

$$\lambda = e^{-\beta A_1}, \quad (41)$$

$$g^{(1)}(\beta, \omega_e, D_e, C) = (1 - \lambda^{N+1})/(1 - \lambda), \quad (42)$$

$$\zeta = \lambda e^{-\beta A_2} \quad (43)$$

and

$$g^{(2)}(\beta, \omega_e, D_e, C) = (1 - \zeta^{N+1})/(1 - \zeta). \quad (44)$$

Also,

$$Q_W^{(1)} < Q_W^{(2)} < Q_W. \quad (45)$$

Differentiating $Q_W^{(1)}$ and $Q_W^{(2)}$ with respect to β we determined $\partial Q/\partial\beta$ and $\partial^2 Q/\partial\beta^2$, which on being substituted into eqs (29) and (30), yielded two somewhat long analytical expressions for entropy as well as thermal capacity each.

8. Numerical calculations for thermodynamic quantities

We have determined values of partition function, entropy and thermal capacity over a reasonably wide range of temperature for H_2 , Li_2 , HF , CO , Cl_2 , ICl and I_2 , assuming their interatomic interactions to be governed by various FP potential energy functions and employing the relevant parameters from tables 1 and 2. With a view to highlight the superiority of the FP potentials, we have also included the results obtained with three-parameter potentials put forward by Morse, Varshni, Levine and Lippincott [2–4], and reproduced below

$$U_M(r) = D_e [1 - e^{-a(r - r_e)}]^2, \quad (46)$$

$$U_V(r) = D_e \left[1 - \frac{r_e}{r} e^{-b_V(r^2 - r_e^2)}\right]^2, \quad (47)$$

$$U_{Le}(r) = D_e \left[1 - \frac{r_e}{r} e^{-b_{Le}(r^p - r_e^p)}\right]^2, \quad (48)$$

and

$$U_{Li} = D_e [1 - e^{-x}] \left[1 - a_{Li} b_{Li} x^{0.5} e^{-b_{Li}(xr/r_e)^{0.5}}\right]. \quad (49)$$

The choice of the molecules has been guided by the coverage of broad range of ω_e and D_e values and the fact that their RKR curves are precisely known. The temperature up to which calculations have been carried out for a particular molecule is such that Boltzmann factor for $E_n > D_e/2$ makes negligible contribution to Q .

We have evaluated the quantities of interest by performing summation of Boltzmann factors or relevant terms pertaining to E_n values determined from the experimental (RKR) data, energy eigenvalues for the Morse and Wei Hua potentials and from the three- or FP potential energy functions mentioned earlier. Besides, computations have also been carried out employing the two sets of analytical expressions corresponding to Wei Hua's potential obtained in §7. These results for different molecules have been projected for $10^j Q$, $10^j S$ and $10^j C$ in tables 8; each table contains data for one molecule. We have used the following symbols to depict various kinds of data in these tables: Experimental reference value (RKR), Morse potential eigenvalues (ME), Morse potential function curve (M), Varshni's function (V), Levine potential function (Le), Lippincott function (Li), Wei Hua's eigenvalue corresponding to eq. (37) (WE), Wei Hua's potential energy function (W), analytical expressions eqs (39) and (40) for Wei Hua's potential (W1 and W2, respectively) and new FP potential functions (I, II and III, respectively).

9. Discussion of results for thermodynamic characteristics

From a perusal of the contents of tables 8 we observe that the values of Q , S and C as predicted by using various methods and potential energy functions do not exhibit a definite trend of relative magnitudes even within broad categories of three-parameter potentials or FP potentials. The sequence of the values is not only different from molecule to molecule

but also for different thermodynamic properties and sometimes even for the same quantities corresponding to different temperatures. For example, in the case of HF, $Q(\text{Li})$ is the smallest while $Q(\text{W})$ is the largest but for CO, $Q(\text{V})$ is the smallest and $Q(\text{WE})$ is the largest at all the temperatures. Also for HF, at 200 K, $Q(\text{WE}) < Q(\text{W1})$ while at 4000 K, $Q(\text{W1}) < Q(\text{WE})$. On the other hand, for this molecule the results for entropy as well as thermal-capacity obtained from U_{III} and U_{W} are, respectively, the lowest and the highest values at all the temperatures. Consequently, we cannot make a general statement like a particular thermodynamic quantity as found by a specific method or a particular potential energy function at any temperature will be less or greater than that obtained by some other technique or potential energy function. However, usually, the results based on the eigenvalues of Morse potential are the closest to those found from the RKR data; the main exception is Cl_2 at all the temperatures considered here. This common tendency of good matching between the ME and the RKR values is understandable because generally the RKR values are generated by supplementing the available experimental data with the eigenvalues of the relevant Morse potential. In addition to this, irrespective of their relative magnitudes the outcome of calculations involving the FP potential energy functions are in better agreement with the RKR values as compared to those obtained with the three-parameter potential energy functions including the Morse potential energy curve. It may be pointed out that even in the case of results of FP potential energy functions the findings corresponding to the eigenvalues of U_{W} generally deviate less from the RKR results, which appears to be a consequence of the fact that U_{W} is a modification of Morse potential and so will be the eigenvalues. In contrast, the potential energy curve of Wei Hua leads to more divergent values as compared to the other FP potential energy curves. It may also be emphasized that the predictions of the FP potential energy functions are in poorer accord with the RKR values at low temperatures than at high temperatures for the same molecule. This is so because at very low temperature only the ground state is occupied while at high temperatures a number of energy states contribute to the thermodynamic properties. In the former, any difference in the value of the ground state energy is reflected in the result and in the latter case, the deviations get averaged out.

Table 9. A comparison of different thermodynamic quantities for three molecules at appropriate temperatures calculated through various approaches with the results of [28, 30]. The findings have been projected in the order Q , S ($\text{JK}^{-1} \text{mol}^{-1}$) and C ($\text{JK}^{-1} \text{mol}^{-1}$). Data from [28] and [30] are given under the column identified with symbol F.

Molecule	Temp. (K)	F	RKR	ME	WE	W1	W2	I	II	III
Li_2	252.8	0.431	0.429	0.431	0.431	0.431	0.431	0.427	0.428	0.436
		3.98	3.93	3.98	4.00	3.90	4.00	3.92	3.93	4.14
		6.23	6.17	6.23	6.25	6.40	5.85	6.17	6.18	6.34
ICl	552.9	0.970	0.968	0.971	0.972	0.972	0.972	0.977	0.977	0.979
		8.83	8.79	8.84	8.86	8.85	8.86	8.91	8.90	8.89
		7.82	7.80	7.83	7.88	7.73	7.96	7.88	7.88	7.84
I_2	308.6	0.970	0.966	0.969	0.969	0.969	0.970	0.974	0.973	0.980
		8.83	8.80	8.82	8.82	8.81	8.81	8.87	8.85	8.94
		7.82	7.93	7.81	7.83	7.71	7.90	7.84	7.83	7.85

In order to compare our computations with the results of other workers, we mention that Amorebieta and Colussi [29] and Fernandez and coworkers [28, 30] used dimensionless parameters rather than performing calculations for specific molecules and at definitely defined temperatures. We have established correspondence of some of the molecules considered here with the results of [28–30] and have listed the pertinent data for the FP potential energy functions in table 9. Our values under ME differ from their results by only in third significant figure, which could be just due to difference in the values used for the standard constants.

Taubmann [25], who used a thermodynamic variation perturbation theory by approximating the Morse potential by a suitable polynomial potential, has given results for vibrational partition function for H₂, CO and I₂. Our findings are identical to his at all the temperatures over the range considered by us. Once again, the difference of 1 or 2 in the third significant figure is understandable as mentioned above.

To conclude we may say that the FP potential energy functions for diatomic molecules proposed by us not only have an edge over other potentials in predicting the spectroscopic constants α_e , $\omega_e x_e$ and D_e but are also reasonably well suited for carrying out numerical study of their thermodynamic characteristics.

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