

## Wei Hua's four-parameter potential: Comments and computation of molecular constants $\alpha_e$ and $\omega_e x_e$

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**Abstract.** The value of adjustable parameter  $C$  in the four-parameter potential  $U(r) = D_e [(1 - \exp[-b(r - r_e)]) / (1 - C \exp[-b(r - r_e)])]^2$  has been expressed in terms of molecular parameters and its significance has been brought out. The potential so constructed, with  $C$  derived from the molecular parameters, has been applied to ten electronic states in addition to the states studied by Wei Hua. Average mean deviation for these 25 states has been found to be 3.47 as compared to 6.93, 6.95 and 9.72 obtained from Levine, Varshni and Morse potentials, respectively. Also Dunham's method has been used to express rotation-vibration interaction constant ( $\alpha_e$ ) and anharmonicity constant ( $\omega_e x_e$ ) in terms of  $C$  and other molecular constants. These relations have been employed to determine these quantities for 37 electronic states. For  $\alpha_e$ , the average mean deviation is 7.2% compared to 19.7% for Lippincott's potential which is known to be the best to predict these values. Average mean deviation for ( $\omega_e x_e$ ) turns out to be 17.4% which is almost the same as found from Lippincott's potential function.

**Keywords.** Four-parameter potential; anharmonicity; rotation-vibration interaction constant; spectroscopic constants; RKR curve.

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### 1. Introduction

A knowledge of exact potential function which governs the interaction between atoms as a function of internuclear distance, is of fundamental importance in a wide variety of fields ranging from gas kinetics to stellar structure. Besides, potential energy (PE) curves provide a good deal of information about the molecular structure. Accordingly, a number of methods have been developed to obtain these curves and the most satisfactory technique for this purpose is RKR method [1–3], which is based on the experimental spectroscopic data. This approach is, however, limited to the region for which the spectroscopic data exist. To overcome this limitation, one resorts to either Dunham method or to analytical functions. In the former, term values are expressed as:

$$T = \sum_{i,j} Y_{i,j} (v + \frac{1}{2})^i J^j (J + 1)^j, \quad (1)$$

where  $v$  and  $J$  are the vibrational and rotational quantum numbers, respectively, and the coefficients  $Y_{i,j}$  are related to spectroscopic constants. The formulation of analytical functions is based on the assumption that bonding potential curves can be fitted to a certain form of algebraic expression. A comparative study of the empirical potential functions by Steele *et al* [4] and by Varshni [5] revealed that of all the three-parameter potential functions those suggested by Morse [6] and Varshni [5] gave small average absolute deviation from the RKR curve with their respective values as 3.68% and 2.31%. Later, Levine [7] proposed a modified form of the potential suggested by Varshni and Shukla [8], which led to a lower (1.99%) value of the average absolute deviation. The corresponding Schrödinger equation can, however, be exactly solved only for Morse function.

Some time back Wei Hua [9], introduced a four-parameter (FP) potential function which apart from the usual three parameters viz.  $\omega_e$ ,  $r_e$ ,  $D_e$ , contains a fourth parameter,  $b$ , which in turn, depends on an adjustable constant  $C$ . The value of  $C$  was chosen to minimize the absolute deviation of the calculated values from the corresponding RKR-values. Wei Hua studied 15 electronic states and found that FP curves fit the RKR curves more closely compared to Morse curves. Moreover, the corresponding Schrödinger equation can be solved exactly for zero and approximately for non-zero total angular momentum [9]. Almost all the researchers who have put forward an empirical potential function including the FP potential or have performed the comparative studies, have confined themselves to the study of simple molecules  $H_2$ ,  $O_2$ ,  $N_2$ ,  $CO$ ,  $NO$ , hydrogen and alkali halides or to alkali oxides. With a view to test the applicability of FP potential to a wider range of molecules, Morsagh [10] carried out their comparative study for diatomic molecules containing sulphur. It was found that for outer wall of the potential curve ( $r > r_e$ ) the average mean absolute deviations from RKR curve for Morse, Varshni, Levine and four-parameter potentials are 1.34%, 2.09%, 2.67% and 0.7%, respectively. Encouraged by the results in respect of FP potential, we have now dwelt upon the significance of the adjustable constant  $C$  and have assessed how faithfully the potential function predicts the values of molecular parameters  $\alpha_e$  and  $\omega_e x_e$ . This communication is an outcome of these efforts.

Before proceeding further it may be mentioned that accuracy of a potential function can be judged in two ways: first by its comparison with the curve obtained from the experimental data and second, by using it to evaluate unused constants and comparing these with the respective experimental data. In the reported work the findings have been subjected to both the tests.

## 2. Potential functions for comparative study

In the present work we have considered only those potential functions for comparative study, which fit more closely to the RKR potential curve [4]. The expressions for these potential functions and parameters  $\alpha_e$  and  $\omega_e x_e$  are as follows:

(i) Morse potential [4,6]

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

$$\alpha_e = \left( \frac{6B_e^2}{\omega_e} \right) \left( \Delta^{\frac{1}{2}} - 1 \right),$$

Wei Hua's four-parameter potential

$$\omega_e x_e = \left( \frac{\omega_e^2}{4D_e} \right); \quad (3)$$

(ii) Varshni potential [5,8]

$$U_V(r) = D_e \left[ 1 - \frac{r_e}{r} e^{-b_v(r^2 - r_e^2)} \right]^2, \quad (4)$$

$$\alpha_e = \left( \frac{6B_e^2}{\omega_e \Delta^{\frac{1}{2}}} \right) \left( \Delta - 2\Delta^{\frac{1}{2}} + 2 \right), \quad (5)$$

$$\omega_e x_e = \frac{B_e}{8} \left( 8\Delta - 12 + 36 - \frac{56}{\Delta^{\frac{1}{2}}} + \frac{48}{\Delta} \right); \quad (6)$$

(iii) Levine potential [7]

$$U_L(r) = D_e \left[ 1 - \frac{r_e}{r} e^{-b_L(r^p - r_e^p)} \right]^2, \quad (7)$$

$$\alpha_e = \left( \frac{6B_e^2}{\omega_e} \right) \left( \frac{3}{4} \Delta^{\frac{1}{2}} - \frac{1}{2} \right), \quad (8)$$

$$\omega_e x_e = \frac{B_e}{8} \left( 8\Delta - 12(p-1)\Delta^{\frac{1}{2}} + 8p^2 + 4 - \left[ \frac{(20p^2 - 12p)}{\Delta^{\frac{1}{2}}} \right] + \frac{12p^2}{\Delta} \right); \quad (9)$$

(iv) Four-parameter potential [9]

$$U(r) = D_e \left[ \frac{1 - \exp\{-b(r - r_e)\}}{1 - C \exp\{-b(r - r_e)\}} \right]^2. \quad (10)$$

The expressions for  $\alpha_e$  and  $\omega_e x_e$  for this potential have been obtained in §3.

Here,  $D_e$  is the dissociation energy,  $r_e$  is the equilibrium bond length and 'a' is related to force constant through

$$k_e = 2D_e a^2 = U''(r_e), \quad (11)$$

with

$$k_e = \mu \omega^2; \quad (12)$$

$$\Delta^{\frac{1}{2}} = ar_e; \quad (13)$$

$$b_v = \frac{\frac{1}{2} (\Delta^{\frac{1}{2}} - 1)}{r_e^2}; \quad (14)$$

$$b_L = \frac{p^{-1} (\Delta^{\frac{1}{2}} - 1)}{r_e^p}; \quad (15)$$

$$p = 2 + \frac{\frac{1}{4} (\Delta^{\frac{1}{2}} - 4) (\Delta^{\frac{1}{2}} - 2)}{(\Delta^{\frac{1}{2}} - 1)}. \quad (16)$$

In order to obtain an analytical expression for  $C$ , we have compared FP potential with five-parameter potential function of Hulburt and Hirschfelder [11] because a potential function with larger number of parameters is more flexible. This gives  $C$  as

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

where

$$x = \frac{1 + F}{ar_e}, \quad (18)$$

$$F = \frac{\alpha_e \omega_e}{6B_e^2}, \quad (19)$$

$$G = \frac{8\omega_e x_e}{B_e} \quad (20)$$

and

$$a = \sqrt{\frac{k_e}{2D_e}}. \quad (21)$$

$C$  has been denoted as  $C_{\text{rel}}$  to distinguish it from the  $C$ , obtained by minimum deviation method adopted by Wei Hua.

The values of  $C_{\text{rel}}$  have been computed for the electronic states studied by Wei Hua using the data listed in table 1 and are compared with  $C$  (columns 2 and 3 in table 2). Value of  $C_{\text{rel}}$  depends on  $B_e$ ,  $\alpha_e$  and  $\omega_e x_e$ , apart from other parameters viz.  $\omega_e$ ,  $r_e$  and  $D_e$ , that are used in almost all the three-parameter potential functions. In other words, the value of  $C_{\text{rel}}$  also depends on the rotational constants. Furthermore, it is observed that a small change in  $\alpha_e$  changes  $C_{\text{rel}}$  significantly while a similar change in other parameters produces small variation. For example, in case of  $Li_2$ , if we change the value of either  $\alpha_e$  or  $\omega_e x_e$ , then the resulting variation in the value of  $C_{\text{rel}}$  due to the latter is nearly one-third that due to the former. Thus,  $C_{\text{rel}}$  is more sensitive to the rotation-vibration interaction constant compared to other parameters involved in the relation. Using (17), values of  $C_{\text{rel}}$  for the electronic states studied by Wei Hua, have been calculated and this, in turn, has been used to calculate the FP potential curve.

Mean square deviations in

$$\Delta Y_j = \frac{\sqrt{(U_j - U_{RKR})^2}}{D_e}, \quad (22)$$

where  $j$  denotes four-parameter (FP), Morse (M), Levine (L), Varshni (V) potential functions, have been calculated for all the cases. The results are projected in table 2. It has been found that the mean square deviations with  $C_{\text{rel}}$  are not far off from the corresponding values derived with  $C$  which makes us to have faith in their correctness. In view of this,  $C_{\text{rel}}$  has been employed to calculate the potential curve for additional ten electronic states (table 3) and deduce the values of  $\alpha_e$  and  $\omega_e x_e$  for a total of 37 electronic states of various molecules including the ones studied by Wei Hua.

Table 1. Experimental molecular constants used in this work.

Molecular State	$r_e$ (Å)	$D_e$ (cm <sup>-1</sup> )	$\omega_e$ (cm <sup>-1</sup> )	$\alpha_e$ 10 <sup>3</sup> (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$\mu_e$	Ref.
Li <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	2.6729	8516.780	351.430	7.040	0.6726	2.6100	3.5080	17,14
Na <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	3.0788	6022.600	159.177	0.873	0.1547	0.7254	11.4949	18,14
K <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	3.9244	4440.000	92.405	0.212	0.0562	0.3276	19.4800	19
Cl <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	1.9872	20276.440	559.751	1.516	0.2442	2.6943	17.4844	20
Cl <sub>2</sub> B <sup>3</sup> Π	2.4311	3341.170	255.3800	2.511	0.1631	4.8000	17.48442	21
I <sub>2</sub> XO <sub>g</sub> <sup>+</sup>	2.6664	12547.335	214.520	0.113	0.0373 <sub>7</sub>	0.6079	63.4522	22,23
IClX <sup>1</sup> Σ <sup>+</sup>	2.3209	17557.600	384.275	0.532	0.1142	1.4920	27.4147	24
IClA <sup>3</sup> Π <sub>1</sub>	2.6850	3814.700	211.030	0.744	0.0852 <sub>g</sub>	2.1200	27.4147	24,25
IClA <sup>3</sup> Π <sub>2</sub>	2.6651	4875.520	224.571	0.674	0.0865	1.8823	27.4147	25
HFX <sup>1</sup> Σ <sup>+</sup>	0.9168	49384.000	4138.320	772.400	20.9557	89.8800	0.9571	26
H <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	0.7416	38297.000	4401.265	3051.300	60.8477	120.6020	0.5039	27
CO X <sup>1</sup> Σ <sup>+</sup>	1.1283	90529.000	2169.813	17.504	1.93137	13.2883	6.8562	14
XeO d <sup>1</sup> Σ <sup>+</sup>	2.8523	693.000	156.832	5.400	0.1456	9.8678	14.2327	28
Cs <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	4.6480	3649.500	42.020	0.022	0.0117	0.0826	66.4527	30
Rb <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	4.2099	3950.000	57.7807	0.055	0.0224	0.1391	42.4559	31
XeO b <sup>1</sup> Σ <sup>+</sup>	2.5480	461.000	113.636	14.593	0.1820	11.8410	14.2651	28
Ar <sub>2</sub> CO <sub>u</sub> <sup>+</sup>	3.5960	465.800	66.820	2.500	0.0652	4.0000	19.9810	16
Ar <sub>2</sub> XO <sub>g</sub> <sup>+</sup>	3.7610	99.500	30.6800	3.641	0.0596 <sub>5</sub>	2.4200	19.9810	16
O <sub>2</sub> X <sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	1.2075	42047.000	1579.247	15.466	1.4456	11.5008	7.9975	15
O <sub>2</sub> b <sub>1</sub> Σ <sub>g</sub> <sup>+</sup>	1.2268	28852.000	1432.775	18.198	1.4004	14.0065	7.9975	29
O <sub>2</sub> A <sup>3</sup> Σ <sub>u</sub> <sup>+</sup>	1.5215	6643.000	815.648	18.053	0.9105	19.8513	7.9975	15
O <sub>2</sub> B <sup>3</sup> Σ <sub>u</sub> <sup>-</sup>	1.6042	8121.000	709.050	11.922	0.8189	10.6100	7.9975	15
O <sub>2</sub> <sup>+</sup> X <sup>2</sup> Π <sub>g</sub>	1.1171	54681.000	1905.335	18.970	1.6905	16.3040	7.9973	25
NO X <sup>2</sup> Π <sub>1/2</sub>	1.1507 <sub>7</sub>	53323.758	1904.204	17.100	1.6719 <sub>5</sub>	14.0750	7.4664	14
NO B <sup>2</sup> Π	1.4167	26544.888	1037.200	12.000	1.0920	7.7000	7.4664	14
N <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	1.0976	78742.304	2358.570	17.318	1.9982	14.3240	7.0015	14
N <sub>2</sub> A <sup>3</sup> Σ <sub>u</sub> <sup>+</sup>	1.2866	29772.23	1460.640	18.000	1.4546	13.8720	7.0015	14
N <sub>2</sub> a <sup>1</sup> Π <sub>g</sub>	1.2203	48974.915	1694.208	17.930	1.6169	13.9490	7.0015	14
N <sub>2</sub> B <sup>3</sup> Π <sub>g</sub>	1.2126	39534.94	1733.390	17.910	1.6374	14.1220	7.0015	14
OH X <sup>2</sup> Π <sub>i</sub>	0.9696	37308.074	3737.76	724.200	18.9108	84.8813	0.9481	14
OHA <sup>2</sup> Σ <sup>+</sup>	1.0121	20412.938	3178.860	786.800	17.3580	92.9170	0.9481	14
Br <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	2.2810	15900.307	325.321	0.318	0.0821	1.0774	39.4591	14
C <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	1.2425	50104.485	1854.710	17.650	1.8198	13.3400	6.0000	14
CO d <sup>3</sup> Δ <sub>i</sub>	1.3696	28368.336	1171.940	17.820	1.3108	10.6350	6.8562	14
CO A <sup>1</sup> Π	1.2353	25617.027	1518.240	23.530	1.6115	19.4000	6.8562	14
COe <sup>3</sup> Σ <sup>-</sup>	1.3840	25391.113	1117.720	17.530	1.2836	10.6860	6.8562	14
COa <sup>3</sup> Σ <sup>+</sup>	1.3523	34887.567	1228.600	18.920	1.3446	10.4680	6.8562	14

**Table 2.** Mean square deviations (22) from the RKR curves for the various potentials for the states studied by Wei Hua.

State	$C^a$	$C_{rel}$	$\Delta Y_L$ (%)	$\Delta Y_V$ (%)	$\Delta Y_M$ (%)	$\Delta Y_{FPC}$ (%)	$\Delta Y_{FPC,rel}$ (%)	$\Delta E_C$ (%)	$\Delta E_{C,rel}$ (%)
$Li_2 X^1\Sigma_g^+$	-0.1460	-0.1298	9.879	8.498	9.952	2.842	2.985	2.576	2.707
$Na_2 X^1\Sigma_g^+$	-0.2024	-0.2031	18.721	16.058	21.372	2.028	2.027	2.878	2.872
$K_2 X^1\Sigma_g^+$	-0.2780	-0.2694	10.448	9.155	13.622	2.034	2.062	1.374	1.409
$Cl_2 X^1\Sigma_g^+$	-0.1097	-0.0910	2.063	2.047	7.628	3.502	3.665	3.105	3.265
$Cl_2 B^3\Pi$	-0.1036	-0.1034	3.971	3.378	7.780	2.258	2.258	2.876	2.874
$I_2 XO_g^+$	-0.1460	-0.1547	1.954	3.416	10.439	2.428	2.474	2.176	2.117
$ICl X^1\Sigma^+$	-0.1000	-0.1020	1.822	1.828	6.842	3.298	3.300	3.306	2.989
$ICl A^3\Pi_1$	-0.1680	-0.1780	3.036	5.452	12.181	1.104	1.244	0.910	0.925
$ICl A^3\Pi_2$	-0.1540	-0.1610	2.171	3.940	10.375	1.260	1.320	0.905	0.882
$HF X^1\Sigma^+$	0.1120	0.1210	4.170	4.313	6.313	3.211	3.245	2.816	2.921
$H_2 X^1\Sigma_g^+$	0.1510	0.1752	5.437	9.986	8.051	3.961	4.153	3.553	3.852
$CO X^1\Sigma^+$	0.0370	0.0460	2.551	3.408	1.210	0.548	0.603	0.292	0.347
$XeO d^1\Sigma^+$	-0.0940	-0.0683	7.478	6.192	7.570	5.183	5.398	5.140	4.957
$Cs_2 X^1\Sigma_g^+$	-0.2949	-0.3114	16.507	14.965	22.449	1.889	2.100	1.601	1.512
$Rb_2 X^1\Sigma_g^+$	-0.2890	-0.2898	10.444	9.271	14.103	2.208	2.207	1.446	1.443

<sup>a</sup>The values are slightly different from those obtained by Wei Hua [9], possibly because of reduced mass which we have taken from ref. 14 for all the molecules.

**Table 3.** Mean square deviations from the RKR curves for additional electronic states.

State	$C_{rel}$	$\Delta Y_L$ (%)	$\Delta Y_V$ (%)	$\Delta Y_M$ (%)	$\Delta Y_{FPC,rel}$ (%)	$\Delta E_{C,rel}$ (%)	$E_{max}/D_e$	Ref. for RKR Potential
$XeO b^1\Sigma^+$	0.5410	20.478	18.962	15.985	5.168	2.984	0.6582	28
$Ar_2 CO_u^+$	0.1105	17.744	16.530	14.136	13.406	10.313	0.7022	16
$Ar_2 XO_g^+$	-0.0223	7.302	5.967	6.881	6.038	2.015	0.9484	16
$O_2 X^3\Sigma_g^-$	-0.0242	1.867	1.998	3.244	2.914	1.745	0.7064	15
$O_2 b^1\Sigma_g^+$	-0.0530	0.419	0.484	1.347	0.851	0.381	0.3870	(b)
$O_2 A^3\Sigma_u^+$	-0.2372	8.994	11.166	18.781	3.758	2.805	0.9849	15
$O_2 B^3\Sigma_u^-$	-0.2500	4.612	5.097	11.171	2.612	0.927	0.9031	15
$O_2^+ X^2\Pi_g$	0.0036	0.968	1.220	0.110	0.094	0.102	0.3330	15
$CO a^3\Sigma^+$	0.0169	7.654	8.274	5.998	5.951	3.820	0.7664	(b)
$N_2 X^1\Sigma_g^+$	-0.0561	2.459	2.095	5.573	4.049	2.787	0.9937	(b)

(b) RKR potential is calculated using LeRoy's computer program [32].

### 3. Derivation of $\alpha_e$ and $\omega_e x_e$

On the basis of wave mechanics Dunham [12] has shown that molecular parameters can be expressed in terms of the derivatives of potential functions if it can be expanded in the form of a power series. Applying this method, we get

$$\alpha_e = [ar_e(1 + C) - 1] \frac{6B_e^2}{\omega_e}, \quad (23)$$

and

$$\begin{aligned} \omega_e x_e &= \frac{h}{8\pi^2 c \mu} a^2 (1 + C + C^2) \\ &= B_e \Delta (1 + C + C^2), \end{aligned} \quad (24)$$

where  $B_e = h/(8\pi^2 c I)$  as obtained from the solution of equation for a rotator. The relation for  $\alpha_e$  is of the same form as obtained by Pekeris [13] using the Morse potential function, viz.

$$\alpha_e = \left[ \left( \frac{\omega_e x_e}{B_e} \right)^{\frac{1}{2}} - 1 \right] \frac{6B_e^2}{\omega_e} = [ar_e - 1] \frac{6B_e^2}{\omega_e}, \quad (25)$$

and that of Lippincott's relation [4] i.e.

$$\alpha_e = \left( \frac{6B_e^2}{\omega_e} \right) AB \Delta^{\frac{1}{2}}, \quad (26)$$

where

$$A = \frac{4}{5} \left( 1 - \frac{1}{B \Delta^{\frac{1}{2}}} \right); \quad (27)$$

and

$$B = 1.065. \quad (28)$$

The expression for  $\omega_e x_e$  is to be compared with

$$\omega_e x_e = \frac{B_e}{8} \left( 3 + 12AB \Delta^{\frac{1}{2}} + 6\Delta + 15A^2 B^2 \Delta - 12AB^2 \Delta \right), \quad (29)$$

obtained from Lippincott's potential function [4].

Values of these two parameters have been calculated for 37 electronic states and are given in tables 4 and 5 for  $\alpha_e$  and  $\omega_e x_e$ , respectively. These tables also include the corresponding experimental values and the values found by employing Morse (3), Varshni (5 and 6) and Lippincott's (25 and 29) potential functions. Values of molecular constants used in these calculations are listed in table 1.

#### 4. Results and discussion

The adjustable constant  $C$  is determined by finding the mean square deviation of the FP potential from the RKR potential curve, which itself is calculated using the molecular parameters  $\omega_e$ ,  $\omega_e x_e$ ,  $\alpha_e$ ,  $r_e$  and  $B_e$  of the individual energy levels [1-3]. Thus, any variation in the parameters from level to level is taken care of and hence most of the variations are

**Table 4.** Comparison of experimental values of  $\alpha_e$  with calculated values and the mean deviations [ $\Delta X = (\alpha_e(\text{exptl}) - \alpha_e(\hat{t})) / (\alpha_e(\text{exptl}))$ ]; where  $\alpha_e(\hat{t})$  stands for,  $\alpha_e(\text{FPC}_{\text{rel}})$ , FP;  $\alpha_e(\text{M})$ , Morse;  $\alpha_e(\text{V})$ , Varshni;  $\alpha_e(\text{L})$ , Lippincott for different electronic states.

State	$C_{\text{rel}}$	$\alpha_e(\text{exptl})$ ( $10^3 \text{ cm}^{-1}$ )	$\alpha_e(\text{FPC}_{\text{rel}})$ ( $10^3 \text{ cm}^{-1}$ )	$\alpha_e(\text{M})$ ( $10^3 \text{ cm}^{-1}$ )	$\alpha_e(\text{V})$ ( $10^3 \text{ cm}^{-1}$ )	$\alpha_e(\text{L})$ ( $10^3 \text{ cm}^{-1}$ )	$\Delta X_{\text{FPC}_{\text{rel}}}$ (%)	$\Delta X_{\text{M}}$ (%)	$\Delta X_{\text{V}}$ (%)	$\Delta X_{\text{L}}$ (%)
$\text{Li}_2 \text{ X}^1 \Sigma_g^+$	-0.1298	7 040	7 875	10 206	9 137	9 097	11.9	45.0	29.8	29.2
$\text{Na}_2 \text{ X}^1 \Sigma_g^+$	-0.2031	0.873	0.972	1.449	1.239	1.282	11.4	66.1	42.0	46.9
$\text{K}_2 \text{ X}^1 \Sigma_g^+$	-0.2694	0.212	0.233	0.394	0.329	0.346	9.9	86.0	55.4	63.5
$\text{Cl}_2 \text{ X}^1 \Sigma_g$	-0.0910	1.516	1.672	1.903	1.585	1.655	10.3	25.5	4.6	9.1
$\text{Cl}_2 \text{ B}^3 \Pi$	-0.1034	2.511	2.439	2.793	2.396	2.412	2.8	11.2	4.6	3.9
$\text{I}_2 \text{ X}^1 \Sigma_g^+$	-0.1547	0.113	0.125	0.154	0.131	0.134	10.1	36.5	15.9	18.1
$\text{ICl X}^1 \Sigma_g^+$	-0.1020	0.532	0.581	0.670	0.561	0.582	9.2	26.0	5.5	9.3
$\text{ICl A}^3 \Pi_1$	-0.1780	0.744	0.788	1.000	0.867	0.865	5.8	34.8	16.5	16.3
$\text{ICl A}^1 \Pi_2$	-0.1610	0.674	0.717	0.893	0.767	0.772	6.4	32.5	13.7	14.4
$\text{HF X}^1 \Sigma_g^+$	0.1210	772.400	801.900	658.200	647.600	593.900	3.8	14.8	16.1	23.1
$\text{H}_2 \text{ X}^1 \Sigma_g^+$	0.1752	3051.300	3502.874	2229.439	4183.994	2161.944	14.8	26.9	37.1	29.1
$\text{CO X}^1 \Sigma_g^+$	0.0460	17 504	17 600	16 440	14 080	14 547	0.5	6.0	19.5	16.9
$\text{XeO d}^1 \Sigma_g^+$	-0.0683	5 400	5 088	5 520	4 932	4 745	5.8	2.2	8.9	12.1
$\text{Cs}_2 \text{ X}^1 \Sigma_g^+$	-0.3114	0.022	0.0238	0.0435	0.0361	0.0381	8.8	98.6	64.7	73.9
$\text{Rb}_2 \text{ X}^1 \Sigma_g^+$	-0.2898	0.055	0.062	0.108	0.0897	0.0947	11.3	95.3	62.4	71.3
$\text{XeO b}^1 \Sigma_g^+$	0.5410	14 593	14 900	9 090	7 910	7 842	2.0	37.6	45.7	46.2
$\text{Ar}_2 \text{ CO}^+$	0.1105	2 500	2 189	1 930	1 670	1 667	12.4	22.6	32.8	33.3
$\text{Ar}_2 \text{ XO}^+$	-0.0223	3 641	3 580	3 685	3 210	3 176	1.6	1.2	11.8	12.7
$\text{O}_2 \text{ X}^3 \Sigma_g^-$	-0.0242	15 466	16 870	17 480	14 500	15 311	8.6	13.0	6.2	0.9
$\text{O}_2 \text{ b}^1 \Sigma_g^+$	-0.0530	18 198	19 500	21 052	17 449	18 364	7.1	15.6	4.1	0.9
$\text{O}_2 \text{ A}^3 \Sigma_u^+$	-0.2372	18 053	18 290	25 870	22 100	22 360	1.3	43.3	22.4	23.9
$\text{O}_2 \text{ B}^3 \Sigma_u^-$	-0.2500	11 922	12 810	18 990	15 920	16 478	7.4	59.3	33.6	38.2
$\text{O}_2^+ \text{ X}^2 \Pi_g$	-0.0036	18 970	19 130	18 880	15 690	16 680	1.7	0.5	17.4	12.2
$\text{NO X}^2 \Pi_1$	-0.0352	17 100	18 180	19 000	15 770	16 600	5.8	11.1	7.7	2.6
$\text{NO B}^2 \Pi$	-0.0371	12 000	13 030	13 802	11 500	12 120	8.3	15.0	4.1	1.0
$\text{N}_2 \text{ X}^1 \Sigma_g^+$	-0.0561	17 318	18 478	20 030	16 710	17 598	6.6	15.6	3.5	1.6
$\text{N}_2 \text{ A}^3 \Sigma_u^+$	-0.0836	18 000	19 250	21 808	18 070	19 030	6.7	21.1	0.4	5.7
$\text{N}_2 \text{ a}^1 \Pi_g$	-0.0157	18 170	18 170	18 610	15 500	16 330	1.0	3.7	13.5	8.9
$\text{N}_2 \text{ B}^3 \Pi_g$	-0.0915	17 930	19 400	22 300	18 490	19 500	8.0	24.6	3.2	8.9
$\text{OH X}^3 \Pi_1$	0.0581	724.200	777.000	703.110	645.100	628.900	7.2	2.9	10.9	13.2
$\text{OH A}^3 \Sigma^+$	-0.0518	786.800	949.600	806.990	650.600	838.700	15.8	20.7	2.5	6.6
$\text{Br}_2 \text{ X}^1 \Sigma_g^+$	-0.1431	0.318	0.350	0.430	0.360	0.377	11.4	36.6	14.9	18.4
$\text{C}_2 \text{ X}^1 \Sigma_g^+$	-0.1013	17 650	18 850	22 180	18 440	19 459	6.5	25.6	4.5	10.2
$\text{CO d}^3 \Delta_1$	0.0398	17 820	18 990	17 930	14 920	15 735	6.6	0.6	16.2	11.7
$\text{CO A}^1 \Pi$	-0.1072	23 530	23 970	28 080	23 300	24 450	4.8	19.9	0.9	3.9
$\text{CO e}^3 \Sigma^-$	-0.0014	17 530	18 530	15 400	12 500	16 249	5.4	5.7	12.1	7.3
$\text{CO a}^3 \Sigma^+$	0.0169	18 920	16 664	16 212	13 608	14 271	12.1	14.3	28.1	24.6



**Table 5.** Comparison of experimental values of  $\omega_e \tilde{x}_e$  with calculated values and the mean deviations [ $\Delta X = (\omega_e \tilde{x}_e(\text{expt.}) - \omega_e \tilde{x}_e(i)) / (\omega_e \tilde{x}_e(\text{expt.}))$ ]; where  $\omega_e \tilde{x}_e(i)$  stands for  $\omega_e \tilde{x}_e(\text{FC}_{\text{rel}})$ , FP;  $\omega_e \tilde{x}_e(M)$ , Morse;  $\omega_e \tilde{x}_e(V)$ , Varshni;  $\omega_e \tilde{x}_e(L)$ , Lippincott;  $\omega_e \tilde{x}_e(\text{exp.})$  using equation 29 for the corresponding electronic states given in table 3.

$\omega_e \tilde{x}_e$ (expt.) cm <sup>-1</sup>	$\omega_e \tilde{x}_e$ (FP) cm <sup>-1</sup>	$\omega_e \tilde{x}_e$ (M) cm <sup>-1</sup>	$\omega_e \tilde{x}_e$ (V) cm <sup>-1</sup>	$\omega_e \tilde{x}_e$ (L) cm <sup>-1</sup>	$\omega_e \tilde{x}_e$ (exp) cm <sup>-1</sup>	$\Delta X_{\text{FP,C}_{\text{rel}}}$ (%)	$\Delta X_M$ (%)	$\Delta X_V$ (%)	$\Delta X_L$ (%)	$\Delta X_{\text{exp}}$ (%)
2.6100	3.2150	3.6250	3.9500	2.9708	3.1835	23.1	38.8	16.1	13.8	21.9
0.7254	0.8816	1.0518	0.8640	0.8468	0.8585	21.5	45.0	19.1	16.7	18.3
0.3276	0.3859	0.4808	0.3918	0.3814	0.3700	17.8	46.8	19.6	16.4	12.0
2.6943	3.5437	3.1681	3.1681	2.9890	3.5272	31.5	43.4	17.6	10.9	30.9
4.8000	4.4261	4.8800	4.0982	3.7199	4.3991	7.8	1.7	14.6	22.5	8.3
0.6079	0.7973	0.9169	0.7637	0.7016	0.7860	31.2	50.8	25.6	15.4	29.3
1.4920	1.9104	2.1026	1.7328	1.6202	1.8992	28.01	40.9	16.1	8.6	27.3
2.1210	2.4911	2.9185	2.466	2.2206	2.4423	17.4	37.6	16.3	4.7	15.5
1.8823	2.2354	2.5859	2.1712	1.9709	2.2002	18.8	37.4	15.3	4.7	16.9
89.8800	98.4446	86.6965	75.3269	72.8732	97.8364	9.5	3.5	16.2	18.9	8.8
120.6020	152.4790	126.4533	148.9109	117.6726	150.6605	26.4	4.9	23.5	2.4	24.9
13.2883	13.6250	13.0016	13.6854	10.4741	13.6117	2.5	2.2	19.6	21.2	2.4
9.8678	8.3081	8.8731	7.7068	6.7091	8.2869	15.8	10.0	21.9	32.0	16.0
0.0826	0.0950	0.1209	0.09848	0.09510	0.8858	15.1	46.5	19.3	15.2	7.3
0.1391	0.1678	0.2113	0.1721	0.1668	0.1581	20.6	51.9	23.7	19.9	13.6
11.8410	12.8083	7.0028	5.9355	5.3070	11.9983	8.2	40.9	49.8	55.1	1.3
4.0000	2.6900	2.3960	2.0304	1.8202	2.6742	32.8	44.1	49.2	54.5	33.1
2.4200	2.3130	2.3649	2.0126	1.7960	2.3124	4.4	2.3	16.8	25.7	4.4
11.5008	14.4758	14.8287	12.0728	11.6615	14.4715	25.9	28.9	4.9	1.4	25.8
14.0065	16.8908	17.7877	14.5104	13.8627	16.8654	20.6	26.9	3.6	1.0	20.4
19.8513	20.5039	25.0369	20.9516	19.1156	19.7470	3.3	26.1	5.5	3.7	0.5
10.6100	12.5700	15.4769	12.758	11.9120	12.0516	18.4	45.8	20.2	12.3	13.6
16.3040	16.6684	16.5940	13.5247	13.0900	16.6683	2.2	1.8	17.0	19.7	2.2
14.0750	16.1025	16.9990	13.5732	13.1284	16.0920	14.4	20.7	3.6	6.7	14.3
7.7000	9.4823	10.1317	8.0125	7.7847	9.4755	23.1	31.6	4.1	1.1	23.1
14.3240	16.7209	17.6615	14.3895	13.9912	16.6926	16.7	23.3	5.3	2.3	18.7
13.8720	16.5410	17.9149	14.6094	13.9800	16.4767	19.2	29.1	0.5	0.8	16.5
13.9490	14.4239	14.6521	11.9364	11.5933	14.4221	3.4	5.0	14.4	16.9	3.4
14.1220	17.4174	18.9990	15.4808	14.8614	17.3355	23.3	34.5	9.6	5.2	22.7
84.8813	99.3482	93.6181	79.0097	77.2874	99.1933	17.0	10.3	6.9	8.9	16.8
92.9170	117.6646	123.7592	101.4363	99.3160	117.4958	26.6	33.1	9.2	6.9	26.4
1.0774	1.4596	1.6640	1.3753	1.4418	1.4418	35.4	54.4	27.7	18.7	33.6
13.3400	15.5980	17.1638	13.9766	13.5530	15.5071	16.9	28.6	4.8	1.6	16.2
10.6350	12.6026	12.1036	9.8585	9.5680	12.5931	18.0	13.8	7.3	10.1	18.4
19.4000	20.3393	22.4953	18.3891	17.4757	20.2056	1.7	15.9	5.2	9.9	4.1
10.6860	12.2812	12.3005	10.0159	9.7050	12.2812	14.9	15.1	6.3	9.2	14.9
10.4680	11.0015	10.8165	8.8304	8.6160	11.0000	5.1	3.3	15.6	17.7	5.1

absorbed indirectly. On the other hand, the least square fitted values of the parameters are used in the expression for  $C_{\text{rel}}$ . These values of parameters, therefore, do not take care of level to level variations. In spite of this  $C_{\text{rel}}$  is quite close to the value of  $C$  calculated by minimum deviation method. Among the electronic states which were studied by Wei Hua [9] the values of  $C_{\text{rel}}$  are within  $\pm 6\%$  of the values of the  $C$  except for  $\text{Li}_2(X^1\Sigma_g^+)$ ,  $\text{H}_2(X^1\Sigma_g^+)$ ,  $\text{CO}(X^1\Sigma_g^+)$  and  $\text{XeO}(d^1\Sigma^+)$  where the deviations are, respectively, 11%, 15.9%, 24% and 24%. These deviations can be understood from the fact that the molecular constants vary on going to higher energy levels. In  $\text{Li}_2$ ,  $v = 0$  to 4 and  $v > 10$  levels have  $\alpha_e$  values 0.00704 and 0.0077, respectively (corresponding  $\gamma_e$  values are also different). In the case of those electronic states for which complete and accurate data are available,  $C_{\text{rel}}$  is very close to  $C$ ; the differences may be attributed to the fact that in  $C_{\text{rel}}$ , finer interactions are not included.

The mean square deviations of the FP potential with  $C$  (i.e.  $\Delta Y_{\text{FPC}}$ ) and  $C_{\text{rel}}$  (i.e.  $\Delta Y_{\text{FPC,rel}}$ ) from RKR potential curve have been compared in table 2. The mean square deviations are within  $\pm 5\%$  except for those states for which  $C_{\text{rel}}$  departs significantly from  $C$ .

A desirable condition for the acceptance of a potential function is the exact solution of the corresponding Schrödinger wave equation. As discussed by Wei Hua [9], FP potential provides eigenvalues:

$$E_n = \frac{D_e}{4} \left[ 2 + (Q^2 + 1) - \frac{(\rho_c - \bar{n})^2}{t^2} - \frac{(Q^2 - 1)^2 t^2}{(\rho_c - \bar{n})^2} \right] \quad (30)$$

where

$$Q = \frac{1}{C}, t = \frac{2D_e}{\omega_e(1-C)}, \bar{n} = n + \frac{1}{2}, n = 0, 1, 2, 3; \quad (31)$$

$$\rho_c = \text{sign of}(C)\rho \text{ and } \rho = \left[ \frac{1}{4} + (Q^2 - 1)^2 t^2 \right]^2. \quad (32)$$

The mean square deviation of the energy values ( $E_{\text{cal}}$ ) with  $C(\Delta E_C)$  and  $C_{\text{rel}}(\Delta E_{C_{\text{rel}}})$  from the observed levels ( $E_{\text{obs}}$  i.e.  $U_{\text{RKR}}$  values) have been calculated using the above equation and are given in the last two columns of table 2. Corresponding  $\Delta E_C$  and  $\Delta E_{C_{\text{rel}}}$  are very close to each other supporting that  $C_{\text{rel}}$  equals  $C$  within the accuracy of molecular parameters. To reinforce the above conclusions, the mean square deviations viz.  $\Delta Y_j$  and  $\Delta E_{C_{\text{rel}}}$  from the RKR potential have been compared for additional ten states using  $C_{\text{rel}}$  in the FP potential function and the results are compiled in table 3.

Taking  $C_{\text{rel}}$  as the correct value of the  $C$  parameter,  $\alpha_e$  and  $\omega_e x_e$  have been calculated using 23 and 24, for 37 electronic states including those studied by Wei Hua. The FP potential with  $C_{\text{rel}}$  yields  $\alpha_e$  values within  $\pm 15\%$  of the corresponding experimental values. The observed variation is a consequence of uncertainty in the values of the molecular parameters which, in turn, determine the accuracy of  $C_{\text{rel}}$ . It may, however, be pointed out that the results are closer to the experimental values as compared to the ones obtained from Lippincott's potential function (26) which is claimed to be the best potential for predicting the  $\alpha_e$  values [4]. The average mean deviations for FP, Morse, Varshni and Lippincott's potentials are 7.2%, 27.6%, 18.7% and 19.7%, respectively, establishing the supremacy of FP potential over other three-parameter potentials in predicting the  $\alpha_e$  values.

As regards  $\omega_e x_e$  the average mean deviations have been found to be 17.4%, 26.9%, 15.5% and 13.9%, respectively for FP, Morse, Varshni and Lippincott's potential functions. Obviously, the accuracy is not as good as for  $\alpha_e$ . This is perhaps because  $C_{\text{rel}}$  itself is not as much sensitive to  $\omega_e x_e$ . However, the results are better than the Morse potential for which, unlike the Varshni and Lippincott's potential functions, Schrödinger equation is solvable. The calculated values are slightly larger than the experimental values for almost all the molecules. A graph between  $C_{\text{rel}}$  for the individual level and  $r_{\text{max}}$  (corresponding to  $v$ ) reveals that  $C$  increases almost exponentially to large negative values at higher  $v$ . The nature of the curve at large  $v$  and the fact that the factor  $(1 + C + C^2)$  may be approximated to  $e^C (= 1 + C + C^2/2)$  because  $|C| < 1$ , have prompted us to write  $\omega_e x_e$  in the light of eq. 24, as

$$\omega_e x_e = \frac{h}{8\pi^2 c \mu} a^2 e^C. \quad (33)$$

The use of this relation reduces the average mean deviation to 15.9% (column 11 in table 5) which is comparable to the value obtained from Lippincott's potential function.

## 5. Conclusions

The constant  $C$  has been expressed in terms of molecular constants implying that the FP potential manifests the contribution of vibration, rotation, rotation-vibration interaction constants. Furthermore, the potential may be preferred over all the known three-parameter potentials for the prediction of the rotation-vibration interaction constant,  $\alpha_e$  and it yields the value of  $\omega_e x_e$  as good as provided by Lippincott's function which is known to be the best analytical function for its prediction.

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## References

- [1] R Rydberg, *Z. Phys.* **73**, 376; **80**, 514 (1933)
- [2] O Klein, *Z. Phys.* **76**, 221 (1932)
- [3] A L G Rees, *Proc. Phys. Soc. (London)* **5**, 998 (1947)
- [4] D Steele, E R Lippincott and J T Vanderslice, *Rev. Mod. Phys.* **34**, 239 (1962)
- [5] Y P Varshni, *Revs. Mod. Phys.* **29**, 664 (1957)
- [6] P M Morse, *Phys. Rev.* **34**, 57 (1929)
- [7] I N Levine, *J. Chem. Phys.* **45**, 827 (1966)
- [8] Y P Varshni and R C Shukla, *J. Chem. Phys.* **40**, 250 (1964)
- [9] H Wei, *J. Phys.* **B23**, 2521 (1990)  
H Wei, *Phys. Rev.* **A42**, 2524 (1990)

- [10] M R Morsagh, Ph.D. Thesis Panjab Univ. Chandigarh, India (1994)
- [11] H M Hulburt and Hirschfelder, *J. Chem. Phys.* **9**, 61 (1941)
- [12] J L Dunham, *Phys. Rev.* **41**, 713, 721 (1932)
- [13] C L Pekeris, *Phys. Rev.* **45**, 98 (1934)
- [14] K P Huber and G Herzberg, *Molecular spectra and molecular structure IV. Constants of diatomic molecules* (New York: Van Nostrand) (1979)
- [15] Paul H Krupenie, *J. Phys. Ref. Data.* **1** No. 2, 423 (1972)
- [16] P R Herman, Ph. D. Thesis, Univ. of Toronto (1986)
- [17] B Barakat, R Bacis, F Carrot, S Churassy, P Crozet, F Martin and J Verges, *J. Chem. Phys.* **102**, 215 (1986)
- [18] R F Barrow, J Verges, C Effantin, K Hussein and J d'Incan, *Chem. Phys. Lett.* **104**, 179 (1984)
- [19] A J Ross, P Crozet, J d'Incan and C Effantin, *J. Phys.* **B19**, L 145 (1986)
- [20] A E Douglas and A R Hoy, *Can. J. Phys.* **53**, 1965 (1975)
- [21] J A Coxon, *J. Mol. Spectrosc.* **82**, 264 (1980)
- [22] R Bacis, D Cerny and F Martin, *J. Mol. Spectrosc.* **118**, 434 (1986)
- [23] F Martin, R Bacis, S Churassy and J Verges, *J. Mol. Spectrosc.* **116**, 71(1986)
- [24] J A Coxon and M A Wickramaaratchi, *J. Mol. Spectrosc.* **79**, 380 (1980)
- [25] J C D Brand, D Bussieres and A R Hoy, *J. Mol. Spectrosc.* **113**, 388 (1985)
- [26] G Di Lonardo and A E Douglas, *Can. J. Phys.* **51**, 434 (1973)
- [27] R J Spindler, *J. Quant. Spectrosc. Radiat. Transfer* **9**, 597 (1969)
- [28] J D Simmons, A G Maki and J T Hougen, *J. Mol. Spectrosc.* **74**, 70 (1979)
- [29] D L Albritton, W J Harrop, A L Schmeltekopf and R N Zare, *J. Mol. Spectrosc.* **46**, 103 (1973)
- [30] W Weickenmeier, U Diemer, M Wahl, M Raab, W Demtroder and W Muler, *J. Chem. Phys.* **82**, 5354 (1985)
- [31] C Amiot, P Crozet and J Verges, *Chem. Phys. Lett.* **121**, 390 (1985)
- [32] R J LeRoy, *Chemical Physics Research Report*, University of Waterloo (1992)