Prediction of $\omega_e x_e$ from a Four-Parameter Potential Function of Diatomic Molecules

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Abstract: The knowledge of potential energy curves of molecules is essential in order to have clear picture of its energy levels or molecular structure. No analytic potential function for diatomic molecule has been accepted as universal function for all molecules. The Values of $\omega_e x_e$ for eighteen molecular states have been predicted from a four-parameter function. These values are compared with those predicted by eight other potential functions and with observed one.

Keywords: Empirical model, potential function, diatomic molecule, molecular potential function.

INTRODUCTION

The potential energy functions play an important role in understanding the spectroscopy of diatomic molecules. There are different ways to construct the potential energy curves from these functions. When enough spectroscopic data are not available and quantum mechanical models can not be used due to the cumbersome procedures, the empirical functions can be used for a variety of molecules. In these empirical methods all stable potential energy curves are fitted to an algebraic expression. These empirical functions make use of spectroscopic constants which are experimentally accurately known and are used to construct the potential curves. The parameters of the empirical potential functions are determined in terms of the following constants.

k_e – *the force constant*

D_e – *The dissociation energy*

r_e – *the equilibrium bond length*

α_e – *the vibration – rotation constant*

$\omega_e x_e$ – *the anharmonicity constant*

In three parameter functions, the constants α_e and $\omega_e x_e$ are the unused constants whereas in four parameter functions the $\omega_e x_e$ is the unused constant. These unused constants have been predicted for a number of molecules by a number of workers [1-7 and references there in].

The present paper aims at predicting $\omega_e x_e$ from a four-parameter empirical potential energy function [1] for nineteen molecular states used by Steel *et al.* [2]. Their data are useful in this respect that such a large data for nineteen molecular states from seven potential functions is not available elsewhere. The present paper could not be combined with the paper on potential function [1] because of the fact that different molecular states and molecular constants have been used in the two cases. The four-parameter potential function of Rafi *et al.* [1] is:

$$V(x) = D_e[e^{-2ax}f(x) - 2e^{-ax}] + D_e \qquad (1)$$

where

$$f(x) = \frac{1}{2}[\tanh(bx) + e^{-bx} + Sech(bx)] \qquad (2)$$

where $x = r - r_e$, r is the inter-nuclear distance, a and b are defined below.

We use the following relation of Varshni [8] for the prediction of $\omega_e x_e$:

$$\omega_e x_e = \left[\frac{5}{3}(\mathrm{X}r_e)^2 - (\mathrm{Y}r_e{}^2)\right]\frac{B_e}{8} \qquad (3)$$

It will be appropriate to define here first:

i. The dissociation energy (D_e)

$$V(r_e) - V(\infty) = -D_e \qquad (4)$$

ii. The harmonic force constant (k_e)

$$k_e = \frac{d^2V}{dr^2}|_{r=r_e} \qquad (5)$$

iii. The Sutherland parameter (¢)

$$\Delta = \frac{k_e r_e^{\,2}}{2D_e} \qquad (6)$$

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iv. The anharmonic force constants (X and Y)

$$X = \frac{\frac{d^3V}{dr^3}|_{r=r_e}}{k_e} \quad (7)$$

$$Y = \frac{\frac{d^4V}{dr^4}|_{r=r_e}}{k_e} \quad (8)$$

When equations (4)-(8) are used in eq. (1), we get

$$k_e = 2a^2 D_e \quad (9)$$

$$\Delta = a^2 r_e^{\,2} \quad (10)$$

$$Xr_e = -3\sqrt{\Delta}\left(1 + \frac{1}{4}\beta^3\right) \quad (11)$$

$$Yr_e^{\,2} = \frac{1}{2}\Delta(14 + 12\beta^3 + 3\beta^4) \quad (12)$$

where $\beta = \frac{b}{a}$ and is found by knowing the value of 'a' from eq. (10) and 'b' from eq. (11). Calculating the values of Xr_e and $Yr_e^{\,2}$ from eqs. (11) and (12), and taking the equilibrium rotational constant B_e from the Table (**1**), the value of $\omega_e x_e$ for each molecular state can be found from eq. (3).

RESULT AND DISCUSSION

We have predicted $\omega_e x_e$ for 18 molecular states from potential energy functions of ref. [1]. The molecular constants used in the calculations are shown in Table **1**. In order to compare our results with other analytic potential function, we calculate $\omega_e x_e$ for eight of them (Table **2**).

Percent error has also been calculated for each potential function and is given in Table **3**. The results show that each potential function predicts the values of $\omega_e x_e$ of a molecular state differently and no single function is seen to predict the best value of $\omega_e x_e$ for all the states.

The calculations of $\omega_e x_e$ for eighteen states show that the potential function of ref. [1] predicts relatively closer value of $\omega_e x_e$ for most of the states.

CONCLUSION

The potential energy functions usually consists of two terms, repulsive term and attractive term, the repulsive term is usually introduced explicitly by negative power of inter-atomic distance. The potential treated here has uniqueness in a sense that it does not show the two terms explicitly.

Table 1. List of Constants Used in the Calculations of $\omega_e x_e$

Molecule/State	Δ	Xr Xr_e	B_e cm^{-1}	β	Yr_e^2
$H_2/\ X^1\Sigma_g^+$	2.079	-4.7936	60.83931	0.75639	20.9719
$I_2/\ X^1\Sigma_g^+$	24.54	-12.293	0.03701	-0.8842	92.49481
$N_2/\ X^1\Sigma_g^+$	8.707	-8.047	1.99803	-0.71392	45.33216
$N_2/\ A^1\Sigma_g^+$	12.32	-9.207	1.45404	-0.79505	56.47521
$N_2/a^1\Pi_g$	9.049	-8.919	1.618	-0.36023	61.03349
$N_2/B^1\Pi_g$	11.6	-8.805	1.63703	-0.82082	50.60831
$O_2/\ X^3\Sigma_g^-$	10.2688	-8.97	1.44496	-0.64453	58.0432
$O_2/\ B^3\Sigma_U^-$	18.461	-8.743	0.81897	-1.0877	25.4468
$O_2/A^3\Sigma_g^+$	26.369	-10.907	0.914	-1.05312	48.4446
$CO/X^3\Sigma^+$	6.7173	-8.091	1.93099	0.54558	54.45908
$CO/a^3\Delta$	8.7996	-8.792	1.29598	-0.36393	59.28389
$CO/A^3\Pi$	13.91	-9.504	1.61198	-0.84452	57.71337
$CO/e^1\Sigma^-$	9.305	-9.106	1.26604	-0.2704	64.10587
$CO/a^3\Sigma^+$	8.067	-9.365	1.34503	0.73455	79.17502
$NO/X^2\Pi_1$	10.114	-8.863	1.67995	-0.65743	56.38865
$NO/B^2\Pi$	9.015	-7.978	1.12194	-0.77036	43.13896
$OH/X^2\Pi_g$	5.003	-6.713	18.86705	0.11839	35.07229
$OH/A^2\Sigma^+$	7.235	-7.182	17.35799	-0.76052	35.18045
$HF/X^1\Sigma^+$	4.143	-6.719	0.85309	0.73763	40.81756

Table 2. Comparison of Values of $\omega_e x_e$ in cm^{-1}

Molecules/States	Observed	Ref. [4]	Ref. [8]	Ref. [9]	Ref. [10]	Ref. [11]	Ref. [12]	Ref. [13]	Ref. [14]	This work
$H_2/ X^1\Sigma_g^+$	120.82	123.149	178.49	126.55	84.515	116.00	197.73	148.78	117.71	121.761
$I_2/ X^1\Sigma_g^+$	0.6127	0.5903	0.8486	0.9165	0.9039	0.8402	0.4152	0.8715	0.7016	0.737
$N_2/ X^1\Sigma_g^+$	14.188	16.951	17.848	17.413	15.847	15.962	15.693	17.389	13.81	15.632
$N_2/ A^1\Sigma_g^+$	13.851	13.367	17.595	17.928	16.959	16.434	13.289	17.527	13.994	15.413
$N_2/a^1\Pi_g$	13.825	16.298	14.864	14.649	13.3998	13.429	12.907	14.591	11.595	14.470
$N_2/B^1\Pi_g$	15.198	16.26	18.814	19.063	17.8997	17.475	14.626	18.69	14.913	16.084
$O_2/ X^3\Sigma_g^-$	12.073	11.577	14.85	14.852	13.796	13.614	12.204	14.676	11.683	13.737
$O_2/ B^3\Sigma_U^-$	8.0023	8.638	14.362	14.126	14.736	13.866	8.5264	14.475	11.653	10.437
$O_2/A^3\Sigma_g^+$	13.81	10.249	22.476	24.139	23.861	22.127	10.31	18.293	18.453	17.117
$CO/X^3\Sigma^+$	13.295	14.211	13.684	12.978	11.3698	11.896	13.099	13.227	10.458	13.190
$CO/a^3\Delta$	7.624	8.989	11.582	11.414	10.438	10.463	10.06	11.369	9.0343	11.266
$CO/A^3\Pi$	17.251	14.869	21.758	22.428	21.443	20.559	15.393	21.762	17.429	18.705
$CO/e^1\Sigma^-$	9.578	9.616	11.922	11.789	10.822	10.807	10.24	11.654	9.3178	11.725
$CO/a^3\Sigma^+$	11.013	13.624	11.172	10.858	9.7597	9.9527	10.115	10.904	8.6483	11.264
$NO/X^2\Pi_1$	13.097	14.97	17.059	17.004	15.736	15.587	14.242	16.827	13.394	15.651
$NO/B^2\Pi$	7.603	9.076	10.277	10.125	9.3063	9.2816	8.7464	10.057	7.9991	8.827
$OH/X^2\Pi_g$	82.665	81.603	103.22	93.437	77.545	85.651	105.76	98.429	77.162	94.417
$OH/A^2\Sigma^+$	113.85	117.099	131.39	125.64	111.42	115.17	122.92	101.81	100.75	110.197

Table 3. Percent Error in $\omega_e x_e$ for Various Potential Functions

Molecule / State	Ref. [4]	Ref. [8]	Ref. [9]	Ref. [10]	Ref. [11]	Ref. [12]	Ref. [13]	Ref. [14]	This work
$H_2/ X^1\Sigma_g^+$	2.81	47.73	4.74	30.05	3.99	63.66	23.14	2.57	9.05
$I_2/ X^1\Sigma_g^+$	7.07	38.50	49.58	47.53	37.13	32.23	42.24	14.51	20.35
$N_2/ X^1\Sigma_g^+$	8.17	25.80	22.73	11.69	12.50	10.61	22.56	2.66	10.18
$N_2/ A^1\Sigma_g^+$	6.19	27.03	29.43	22.44	18.65	4.06	26.54	1.03	11.28
$N_2/a^1\Pi_g$	6.84	7.51	5.96	3.07	2.86	6.64	5.54	16.13	4.67
$N_2/B^1\Pi_g$	12.83	23.79	25.43	17.78	14.98	3.76	22.98	1.87	5.83
$O_2/ X^3\Sigma_g^-$	0.33	23.00	23.02	14.27	12.76	1.08	21.56	3.23	13.79
$O_2/ B^3\Sigma_U^-$	17.79	79.47	89.02	84.14	73.27	6.55	80.88	45.62	30.42
$O_2/A^3\Sigma_g^+$	8.25	62.75	74.79	72.78	60.22	25.34	32.46	33.62	23.95
$CO/X^3\Sigma^+$	4.44	2.93	2.38	14.48	10.52	1.47	0.51	21.34	0.78
$CO/a^3\Delta$	50.98	51.91	49.71	36.91	37.24	31.95	49.12	18.50	47.78
$CO/A^3\Pi$	3.60	26.12	30.01	24.30	19.18	22.36	26.15	1.03	8.43
$CO/e^1\Sigma^-$	25.50	24.47	23.08	12.99	12.83	6.91	21.67	2.72	22.42
$CO/a^3\Sigma^+$	19.68	1.44	1.41	11.38	9.63	8.15	0.99	21.47	2.28
$NO/X^2\Pi_1$	5.31	30.25	29.83	20.15	19.01	8.74	28.48	2.27	19.50
$NO/B^2\Pi$	5.63	35.17	33.17	22.40	22.08	15.04	32.28	5.21	16.10
$OH/X^2\Pi_g$	6.48	24.86	13.03	6.19	3.61	27.94	19.07	6.66	14.22
$OH/A^2\Sigma^+$	25.43	15.41	10.36	2.13	1.16	7.97	10.58	11.51	3.21

It predicts the potential energy values for a large number of molecules with very low uncertainties [1]. It is a good addition to the existing potential energy function because there is no universal potential function that predicts accurate potential values for all molecules.

The values of $\omega_e x_e$ calculated from potential function of Rafi et. al [1] are compared with the values calculated from other existing potential functions and with the observed ones. It can be seen that no potential function calculates accurately the value of $\omega_e x_e$. The potential used in this work calculates relatively accurate values for a number of molecules. To conclude with, predicting molecular constants from analytic potential functions is tried in literature; the prediction of $\omega_e x_e$ from four-parameter potential function of Rafi *et al*. [1] is an important addition to the spectroscopic data of the diatomic molecules.

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