MODIFIED VARSHNI-SHUKLA POTENTIAL FUNCTION FOR DIATOMIC ALKALI HALIDE MOLECULES

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ABSTRACT. The values of the rotational constants α_e, vibrational constants ω_e and $\omega_e x_e$ and dissociation energies have been calculated for eighteen diatomic alkali halide molecules by using modified form of the Varshni and Shukla potential function. The calculated values are in good agreement with the experimental values and the potential function is compared with the previously suggested potential function.

Different potential energy functions have been proposed for alkali halide diatomic molecules assuming the molecule to be constituted of ions. For earlier developments reference may be made to Rittner (1951) and Varshni (1957).

Rittner (1951) has presented a theory of alkali halide molecules in the spirit of the Born-Mayer lattice theory Varshni and Shukla (1961) have compared the following three functions :

$$U = - \frac{e^2}{r} + Be^{-r/\sigma} \quad \dots \quad \dots \quad \text{(Born-Mayer)} \qquad \dots \quad (1)$$

$$U = - \frac{e^2}{r} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^4} - \frac{2e^2\alpha_1\alpha_2}{r^7} - \frac{C}{r^6} + A \exp\left(\frac{-r}{\rho}\right) \quad \text{(Rittner)} \quad \dots \quad (2)$$

$$U = - \frac{e^2}{r} + P \exp(-kr^2) \qquad \text{(Varshni—Shukla)} \qquad \dots \quad (3)$$

B, σ, A, ρ, P and k are the constants α_1 and α_2 are the polarizability values of the ions.

By a comparative study of these functions Varshni and Shukla (1961) concluded that potential function (3) is superior to potential function (1) but slightly inferior to potential function (2).

However from the study of the calculated values of α_e, the rotational constant, and $w_e x_e$, the vibrational const., we have found that it is possible to account for α_e and $w_e x_e$ more satisfactorily, if we modify the Varshni and Shukla (1961) potential function. The modified form of the function is :

$$U = - \frac{e^2}{r} + P \exp\left(-kr^{3/2}\right) \qquad \dots \quad (4)$$

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The constants P and k can be determined by using the following conditions :

$$\left(\frac{dU}{dr} \right)_{r=r_e} = 0 \qquad \qquad \dots \text{ (5)}$$

$$\left(\frac{d^2U}{dr^2} \right)_{r=r_e} = k_e, \qquad \qquad \dots \text{ (6)}$$

where k_e is the force constant and r_e, is the equilibrium internuclear distance. The calculations for α_e and $\omega_e x_e$ and D_i the dissociation energies have been made. The method of calculating α_e and $\omega_e x_e$ has been explained by Varshni (1957-59). The relevant equations are :

$$\alpha_e = - \left[\frac{Xr_e}{3} + 1 \right] \frac{6B_e^2}{\omega_e} \qquad \qquad \dots \text{ (7)}$$

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

where $\qquad W = 2.1078 \times 10^{-16}$,

$\qquad\qquad X = U'''(r_e)/U''(r_e)$ and $Y = U^{IV}(r_e)/U''(r_e)$.

and $\qquad\qquad D_i = - U(r_e)$.

The experimental data are the same as those used by Varshni and Shukla (1961).

The values of α_e and $\omega_e x_e$ and D_i calculated by using the function (4) have been presented in tables I, II, and III. α_e and $\omega_e x_e$ and D_i values calculated by Varshni and Shukla (1961) from potential functions (2) and (3) have also been included in tables I, II, and III for comparision.

CONCLUSION

α_e : table (I) shows that a considerable improvement is obtained over the values calculated by using Varshni and Shukla potential function. In certain cases e.g. LiBr, NaCl, NaBr, NaI, KI etc., the values are rather better than the values calculated from Rittner's function. In some cases, the values are as good as those obtained from Rittners function.

However the proposed function is slightly inferior to Rittner's function in certain cases such as, RbCl, RbBr, etc. It is interesting to note that the proposed function fails miserably in the case of flourides. Excluding fluorides the percentage error is less than the Rittner's function.

TABLE I

The rotational constants

Molecule	$\alpha_e \times 10^4$ obs. cm^{-1}	$\alpha_e \times 10^4$ Calc. Pot (2) cm^{-1}	% error	$\alpha_e \times 10^4$ Calc. Pot (3)	% error	$\alpha_e \times 10^4$ Calc. Pot (4)	% error
LiF	(a) 197.1	145.3	−26.3	100.7	−48.9	85.35	—
LiBr	(b) 56.41	50.41	−10.6	47.63	−15.6	57.33	+ 1.6
LiI	(b) 40.90	37.6	− 8.1	37.05	− 9.4	44.04	+· 7.7
NaCl	(b) 16.1	14.9	− 7.5	13.81	−14.2	16.04	− 0.4
NaBr	(b) 9.4	11.0	+17.0	8.45	−10.1	9.727	+3.5
NaI	(b) 6.5	7.67	+18.0	6.10	− 6.2	7.003	7.7
KF	(c) 23.35	19.91	−14.7	16.54	−29.2	2.015	—
KCl	(b) 7.90	7.70	−2.5	7.37	− 6.7	8.330	+ 5.4
KBr	(b) 4.05	3.87	− 4.4	3.67	− 9.4	4.185	+ 3.2
KI	(b) 2.70	2.51	− 7.0	2.37	−12.2	2.731	+1.1
RbF	(d) 15.18	14.49	− 4.5	13.61	−10.5	22.95	—
RbCl	(b) 4.50	4.42	− 1.8	4.29	− 4.7	4.833	+ 7.3
RbBr	(b) 1.86	1.83	− 1.6	1.80	− 3.2	2.033	+ 9.1
RbI	(b) 1.10	1.04	− 5.5	1.00	− 9.1	1.145	+ 3.6
CsF	(b) 11.00	12.49	+13.5	12.96	+17.8	14.34	—
CsCl	(b) 3.30	3.38	+ 2.4	3.41	+ 3.3	3.802	+15.16
CsBr	(b) 1.20	1.19	− 0.8	1.17	− 2.5	1.274	+ 6.2
CsI	(b) 0.68	0.75	+10.3	0.72	+· 5.9	0.8085	+17.65
Average %error excluding flourides			7.0%		8%		6.4%

(a) Vidale (1960) ; (b) Honig *et at.* (1954) ! (c) Green *et al.* (1958) ! (d) Lew *et al.* (1958).

TABLE II

The vibrational constants

Molecules	$\omega_e x_e$ est. Cm⁻¹.	$\omega_e x_e$ Calc. Pot. (2) cm⁻¹	$\omega_e x_e$ Calc. Pot. (3) cm⁻¹	$\omega_e x_e$ Calc. Pot. (4) cm⁻¹
LiF	7.9(a)	6.896	6.62	4.826
LiBr	4.28(b)	3.66	4.12	4.373
LiI	3.35(b)	2.997	3.49	3.694
NaCl	2.05(b)	1.75	1.89	—
NaBr	1.50(b)	1.64	1.39	1.464
NaI	1.08(b)	1.25	1.10	1.163
KF	1.45(c)	1.99	1.96	2.075
KCl	1.30(b)	1.21	1.32	1.41
KBr	0.80(b)	0.727	0.792	0.8341
KI	—	0.507	0.553	0.5855
RbF	1.3(c)	1.95	2.09	18.4
RbCl	0.92(b)	0.83	0.916	1.08
RbBr	—	0.465	0.520	0.5512
RbI	—	0.292	0.323	0.7149
CsF	1.23(c)	1.97	2.31	2.39
CsCl	0.75(b)	0.722	0.824	0.8654
CsBr	—	0.335	0.374	0.373
CsI	—	0.208	0.229	0.249

(a) Vidale (1960) ; (b) Klemperer (1957), Rice (1957) ! (c) Barrow et. al. (1953).

$\omega_e x_e$: In table II, except for LiF, the reported values are estimated ones and it is not possible to draw any conclusions regarding the errors of the calculated results from the potential functions considered. Hence we have not given the percentage errors.

The values of $\omega_e x_e$ calculated with potential functien (4), are nearer to the estimated values than those calculated by using Rittner's and Varshni-Shukla's functions in many cases,

TABLE III

The dissociation energies

Mole cules	D_i observed* Kcal/mole	D_i Pot (2) Kcal/mole	% error	D_i Calc. from Pot (3) Kcal/mole	% error	D_i Calc. from Pot (4) Kcal/mole	% error
LiF	177.8	185.8	4.5	184.0	3.5	174.8	1.7
LiBr	142.1	142.1	0.4	132.7	7.0	133.9	6.2
LiI	130.7	130.6	0.1	123.0	5.9	122.0	6.7
NaCl	127.9	130.0	1.6	125.5	1.9	124.6	2.6
NaBr	124.4	127.7	2.7	118.8	4.5	117.9	5.2
NaI	114.5	118.9	3.8	109.8	4.1	109.0	4.8
KF	131.6	136.5	3.7	134.7	2.4	133.4	1.4
KCl	133.3	116.2	2.6	112.2	1.0	111.5	1.6
KBr	109.1	109.5	0.4	105.8	3.0	105.1	3.7
KI	101.9	101.1	0.8	97.5	4.3	96.97	5.0
RbF	135.8	135.7	0.1	131.8	2.9	141.7	4.3
RbCl	111.1	111.4	0.3	107.5	3.2	106.9	3.8
RbBr	106.7	106.0	0.7	102.0	4.4	101.5	4.8
RbI	98.7	97.6	1.1	94.0	4.8	93.3	5.5
CsF	133.3	135.4	1.6	128.9	3.3	128.2	3.8
CsCl	107.6	108.1	0.5	103.6	3.7	103.0	4.3
CsBr	103.2	101.3	1.8	97.5	5.5	97.2	5.8
CsI	93.2	88.3	5.3	85.4	8.4	84.9	8.9
Average % Error			1.8		4.1		4.6

*Gaydon (1953).

D_i : It is found from table III that % error in D_i values calculated by using pot. (4) is slightly greater than those calculated by using Rittner's and Varshni Shukla's potential function.

However, it should be noted that most of the experimental values are uncertain by above ± 4 k cal/mole, which corresponds to 3% hence no strict conclussion can be drawn about the relative performances.

To summarize, we may say that the results of α_e and $\omega_e x_e$ obtained with potential function (4) are superior to potential functions. (2) and (3).

From the discussion for the repulsive term by Varshni-Shukla (1961) we retain the conclusion drawn by them that the exponential term in Fn. (4) represents the combined effect of polarization and Van der Waal forces.

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REFERENCES

Barrow R. F. and Caunt, A. D. 1953, *Proc. Roy. Soc. (London),* A**219,** 120.

Caydon A. G., 1953. *Dissociation Energies and Spectra of Diatomic Molecules* Chapman and Hall, Ltd., London

Green, G. W., Low. H. *Can. J. Physics.* 1958, 36, 171, *Phys. Rev.* **96,** 629.

Honig, A. Mandel, M. Stitch M. L. and Townes C. H. 1954, *Phys. Rev.* **96,** 629.

Klemperer W. and S. A. Rice. 1957, *J. Chem., Phys.* **26,** 618.

Low, Morris, Geiger, and Esinger. 1958, *Can. J. Phys.* **36,** 171.

Rice S. A. and W. Klemperer, 1957, *J. Chem. Phys.,* **27,** 573.

Rittner E. S., 1951, *J. Chem. Phys.,* **19,** 1030.

Varshni, Y. P., 1957, *Revs. Modern Phys.* **29,** 664 ; 1959, 31, 839.

————— 1957, *Trans. Faraday Soc.* **53,** 132.

————— and Shukla R. C. 1961, *J. Chem. Phys.* **35,** 582.

Vidale, G.L., 1960, *J. Phys. Chem.* **64,** 314.