

Potential Energy Curves of Alkali Halide Diatomic Molecules

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R. K. R. curves have been constructed for the ground state of alkali halide diatomic molecules and compared with the well behaved empirical potential function. It is found that the modified form of Rittner's potential accurately reproduces the R. K. R. curves.

Potential energy curves for different electronic states of diatomic molecules are of fundamental importance in understanding a number of molecular phenomena viz. dissociation energies, perturbations etc. In addition, these curves form a basis for the discussion of the nature of binding in different states of a molecule. Thus, a comparison of experimental potential curves with theoretical curves can help in deciding the ionicity or polarity of the chemical bond. Even though the potential energy curves of a large number of diatomic molecules, in their various electronic states, have been constructed from experimental data, only a few serious attempts have been made so far in the above direction (VARSHNI and SHUKLA^{1,2}, GOHEL³, THAKUR et al.⁴). Work on alkali halides has been done only in the context of Dunham's theory as put in practice by VARSHNI⁵.

A more stringent test of an empirical potential function lies in the comparison of the $U(r)$ versus r dependence with the curves as determined from the R. K. R. method. Although this method is now well known, no extensive comparisons have been made for alkali halides. The quality and the quantity of the experimental data now available is considerable and enables to carry out such comparisons.

We have chosen six well behaved empirical functions for this comparison. After careful consideration of all proposed ionic functions known to us, we have selected the following for consideration:

BORN-MAYER⁶, RITTNER⁷; V-S-4 ($p = \frac{3}{2}$)^{2,8}, Modified Rittner (FINN⁹, GOHEL^{3,10,11}); GOHEL-TRIVEDI¹²; and V-S-3² with n treated as a variable parameter.

The analytical forms of these potential functions are given in Table 1. The spectroscopic data needed for the evaluation of the parameters of the potential functions have been taken from VARSHNI and SHUKLA².

Calculations

The R.K.R. method used in the calculations of the experimental potential curves was originally suggested by RYDBERG¹³ and KLEIN¹⁴ and later modified by REES¹⁵ and VANDERSLICE et al.¹⁶. This method is a WKB procedure in which we start with the experimental energy levels and find out the classical turning points. JARMAIN¹⁷ has obtained the expressions for the classical turning points in terms of power series in $(v + \frac{1}{2})$ in which the coefficients of

Table 1.

No.	Potential function	Analytical expression
1.	BORN-MAYER	$U(r) = -\frac{e^2}{r} + A \exp(-r/p)$
2.	RITTNER	$U(r) = -\frac{e^2}{r} + A \exp(-r/p) - \frac{e^2(\alpha_1 + \alpha_2)}{2r^4} - \frac{2e^2\alpha_1\alpha_2}{r^7} - \frac{c}{r^6}$
3.	V-S-4	$U(r) = -\frac{e^2}{r} + A \exp(-k r^p); \quad p=3/2$
4.	Modified RITTNER	$U(r) = -\frac{e^2}{r} + A \exp(-r/p) - \frac{\alpha_{av}}{r^4}$
5.	GOHEL-TRIVEDI	$U(r) = -\frac{e^2}{r} + \frac{A}{r} \exp(-k r^2)$
6.	V-S-3	$U(r) = -\frac{e^2}{r} + A r^n \exp(-r/p), \quad n \text{ as variable parameter.}$



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different powers of $(v + \frac{1}{2})$ include the spectroscopic constants. DAVIS and VANDERSLICE¹⁸ have established the validity of the Jarman series. In the present investigation we have used JARMAIN's method¹⁷ to construct the potential energy curves of alkali halide molecules.

It should be noted that for all alkali halides the experimental data are accurately known for the first three or four vibrational levels and hence we have constructed the curves for the first three vibrational levels only.

Results and Discussion

The results of this comparative study are shown in Table 2 for NaCl. Similar results have been obtained for all alkali halide molecules.

For both turning points of the $v = 0 - 3$ levels, the modified Rittner potential represents the curve quite accurately. Although all ionic potential functions reproduce the experimental curve with reasonable accuracy, an additional feature is observed in the case of the modified form of Rittner's potential. This potential gives correct and equal energies for both

turning points of a given vibrational level. The other potentials fail to do so. The examination of Table 2 brings out the following interesting behaviour of the different potential functions.

The Born-Mayer potential gives low energy values for $r < r_e$ and high ones for $r > r_e$.

Rittner's potential gives high energy values for $r < r_e$ and low ones for $r > r_e$. V-S-4 ($p = \frac{3}{2}$) is a good representation for $r < r_e$ but for $r > r_e$, the predicted values are lower than the experimental values.

The Gohel-Trivedi function gives high energies for $r < r_e$ and lower energies for $r > r_e$.

The V-S-3 potential seems to be good for $v = 0$ and 1, but it predicts low energies for all values of r . Hence the modified Rittner potential seems to be best among all potentials considered in the present study.

Also, the present study shows that the R. K. R. curve calculated even in a small region of r near r_e (the equilibrium distance) can be used to compare empirical potential functions which predict very similar lower order spectroscopic constants in the context of Dunham's method.

Table 2.

v	Turning points (Å)	R. K. R. (cm ⁻¹)	BORN-MAYER	RITTNER	Modified RITTNER	V-S-4	G-T	V-S-3
3	2.6107	1254.6	1226.8	1270.3	1253.7	1251.2	1264.5	1246.1
2	2.5672	900.54	833.85	910.55	900.06	899.26	907.56	896.11
1	2.5163	542.91	535.33	547.91	542.75	542.83	546.86	541.38
0	2.4471	181.88	180.43	182.93	181.88	181.96	182.77	181.72
0	2.2834	181.88	183.17	180.67	181.88	181.40	180.51	181.72
1	2.2317	542.91	549.36	536.46	542.91	538.71	535.57	541.54
2	2.1983	900.54	913.94	887.08	900.55	893.77	884.01	896.75
3	2.1725	1254.6	1276.4	1231.00	1254.9	1242.9	1226.6	1247.7

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