On the Modified Form of Rittner's Potential Function

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The modified form of the Rittner's potential function has been tested in it's ability to reproduce the $\omega_e x_e$ values of alkali halide diatomic molecules. The function has been compared with the original form of Rittner's potential. The comparison of the calculated values of $\omega_e x_e$ with those obtained experimentally shows that the modified form of the Rittner's potential is better than the original one. The reliability of the test made in the present study has been briefly discussed.

Introduction

A large number of workers have studied the potential energy functions of ionic molecules such as alkali halides. For earlier developments reference may be made to RITTNER[1] and VARSHNI[2]. The systematic study of ionic potential functions began with RITTNER[1] who could combine better experimental data with the theory. VARSHNI[2] and VARSHNI and SHUKLA[3] pointed out that the repulsive constants are not the same for all the ionic molecules. Before Varshni and Shukla proposed their potential function with a gaussian form of the repulsion term, use was made of Rittner's potential and the simple Born-Mayer potential. Although the function proposed by Varshni and Shukla was found to be slightly inferior to Rittner's potential, it has the credit of simulating the polarization and Van der Waals effects in a single term and hence reducing the labour involved in the calculations of different physical parameters. This model has been improved by GOHEL[4] who showed that the improved model is almost as good as that of Rittner.

Although Rittner's function is a fairly good representation of the potential energy of the alkali halide diatomic molecules, there are some difficulties in the use of this potential. For example, the reliable values of the polarizability of the constituent ions are not known accurately in the molecular environment. Secondly, it has been observed that the use of higher order multipole interaction terms impairs the situation (KLEMPERER et al.[5]). Purely on theoretical basis there can be nothing which can prevent the inclusion of the higher order interaction terms in Rittner's potential. VARSHNI and SHUKLA[6] showed that Rittner's potential can not be used for alkali hydrides. Moreover, for many ionic molecules such as group III monohalides, the polarizability values of the single charged positive ions are not known. There are also some anomalies as regards the polarizability of the negatively charged hydrogen ion (KLEMPERER and MARGRAVE[7], ALTSHULLER[8]). Noticing these facts and taking considerations of the secondary forces, GOHEL[9] applied the modified form of Rittner's potential to the alkali hydrides and group III monohalides (see also FINN[10]).

A single potential function, applicable to a large number of molecules having the same type of chemical bond, has always been desirable. The empirical potentials are not only useful in systematizing the spectroscopic data, but they can be much more convenient in calculating the vibrational wave functions (CASHION[11]). In the case of alkali halides the true nature of the potential curves of excited electronic states is not known accurately. The ground state potential energy curve can be used with the data of absorption spectroscopy to construct the potential curves of the excited states (DAVIDOVITS and BRODHEAD[12]). Hence it is desirable to have an accurate potential function for the ground electronic state. It is the purpose of the present paper to test the applicability of the modified from of Rittner's function to alkali halide diatomic molecules. The successful application of this potential to alkali hydrides and group III monohalides led the authors to such a study. It was also desired to compare two sets of experimental values of $\omega_e x_e$.

Calculations

The merit of a potential function used for representing the potential energy of a diatomic molecule

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must be judged principally by the agreement between the eigenvalues it predicts and the spectroscopically observed term values. VARSHNI[13] has used an aproximate method to compare the class of three parameter potential functions which can be specified by the dissociation energy D_e, the fundamental frequency ω_e and the equilibrium internuclear distance r_e. It is based on two approximate formulae derived by DUNHAM[14], which give the spectroscopic constants α_e and $\omega_e x_e$ in terms of the derivatives of the potential function evaluated at r_e. Since the constants D_e, ω_e, B_e, $\omega_e x_e$ and α_e give the most important contributions to the eigenvalues, this method certainly gives a valid and useful comparison.

In the present paper we have calculated $\omega_e x_e$ values from the modified form of Rittner's potential and compared them with those calculated from Rittner's original potential and those obtained experimentally. Since the experimental values of the dissociation energy for alkali halides are uncertain by about 3%, it was thought necessary to specify the potential by r_e, ω_e and α_e.

The modified form of Rittner's potential is represented as

$$U = -\frac{e^2}{2} + A \exp\left(-\frac{r}{\varrho}\right) - \frac{\alpha_{av}}{r^4}. \tag{1}$$

Here A, ϱ, and α_{av} are the potential parameters which can be determined by using the following equations.

$$\left(\frac{dU}{dr}\right)_{r_e} = 0, \tag{2}$$

$$\left(\frac{d^2U}{dr^2}\right)_{r_e} = k_e, \quad \text{the force constant} \tag{3}$$

$$\alpha_e = -\left[\frac{x_3 r_e}{3} + 1\right] \frac{6 B_e^2}{\omega_e}, \tag{4}$$

and

$$x_3 = \left(\frac{d^3U}{dr^3}\right)_{r_e} \Big/ \left(\frac{d^2U}{dr^2}\right)_{r_e}. \tag{5}$$

The $\omega_e x_e$ values have been calculated from the expression

$$\omega_e x_e = [\tfrac{5}{3} x_4^2 - x_3] \frac{W}{\mu_A r_e^2} \tag{6}$$

where

$$x_4 = \left(\frac{d^4U}{dr^4}\right)_{r_e} \Big/ \left(\frac{d^2U}{dr^2}\right)_{r_e}. \tag{7}$$

μ_A is the reduced mass of the molecule and W has been defined by VARSHNI[2].

Results and Discussion

The experimental and theoretical values of $\omega_e x_e$ have been collected in Table 1. The second and third columns of this table give experimental values of $\omega_e x_e$, obtained from microwave and infrared spectra of the alkali halides respevtively. It is interesting to note that in almost all cases $\omega_e x_e$ (I.R.) is greater than $\omega_e x_e$ (M.W.). The difference between the $\omega_e x_e$ values of the two sets decreases as we go to heavier molecules.

Table 1. $\omega_e x_e$ values in cm^{-1}.

Molecule	Experimental values		Calculated with Rittner's Potential	Calculated with modified Rittner's Potential
	Microwave	Infrared		
LiF	8.895	7.9	8.155	7.978
LiCl	—	4.2 ± 0.3	4.405	4.85
LiBr	3.88	4.28	3.601	3.866
LiI	3.1 ± 0.1	3.39	3.049	3.154
NaF	3.4	—	3.277	2.582
NaCl	1.755	2.05	1.780	1.890
NaBr	1.16	1.50	1.245	1.296
NaI	0.964	1.08	0.999	1.001
KF	2.4	1.45	2.319	2.493
KCl	1.176	1.30	1.207	1.226
KBr	0.758	0.80	0.778	0.785
KI	0.574	—	0.604	0.593
RbF	0.75	1.3	1.780	1.871
RbCl	0.856	0.92	0.882	0.875
RbBr	0.463	—	0.490	0.483
RbI	0.335	—	0.351	0.339
CsF	0.73	1.23	1.721	1.554
CsCl	0.74	0.75	0.761	0.700
CsBr	0.3602	—	0.393	0.379
CsI	0.2542	—	0.271	0.265

In a systematic study of the comparison of the $\omega_e x_e$ values obtained through microwave spectra and those obtained through infrared spectra, CLOUSER and GORDY[15] have shown that $\omega_e x_e$ values obtained from infrared spectra are the reliable ones. It is interesting to compare our values with both sets of experimental values.

For LiF, the modified potential yields almost the value of $\omega_e x_e$ (I.R.). For LiCl, the original form of the Rittner's potential is found to give a better value of $\omega_e x_e$. For LiBr, the $\omega_e x_e$ (M.W.) is 3.88 cm^{-1} (CLOUSER and GORDY[15]), while there are two infrared values given in the literature. KLEMPERER and RICE[16] give 4.28 cm^{-1}, while KLEMPERER et al.[5] give 3.53 ± 0.15. The value obtained form the modified Rittner's potential is nearer to that of KLEMPERER and RICE[16] and that of CLOU-

SER and GORDY[15]. CLOUSER and GORDY[15] have pointed out that the $\omega_e x_e$ values of KLEMPERER and RICE[16] are the reliable ones. In this connection the modified potential is better than the original one. For LiI, $\omega_e x_e$ (M.W.) is $3.1 \pm 0.1\ \text{cm}^{-1}$, while $\omega_e x_e$ (I.R.) is $4.28\ \text{cm}^{-1}$. The modified form of the potential gives better agreement with the I.R. value. For NaF, the original form of the potential seems better. For NaCl, NaBr, NaI, KF, KCl and KBr the $\omega_e x_e$ values obtained by the modified form of the potential are in better agreement with the I.R. values. For KI the I.R. values are not available, however, the value calculated from the modified form seems quite reasonable. For RbF, again, none of the calculated values agrees with the experimental one. For RbCl the original form seems better. As we move further in the table, we find that the difference between the I.R. and M.W. values goes on decreasing. In the light of this fact the $\omega_e x_e$ values of the Rb and Cs halides, except for RbCl and CsCl, calculated from the modified form of the Rittner's potential seem better than those from the original form of the Rittner's potential. The over all behaviour of the modified form of the potential seems better.

Conclusion

Rittner's original potential function is a two-parameter potential function, while the modified function is a three-parameter potential with necessarily the same character as that of Rittner's original function. It is, therefore, not too surprising that the modified form gives more reliable results. However, the three parameters in the modified form are determined by r_e, ω_e and α_e. It therefore is undoubtly a better representation of the true potential than the original form. For nonionic molecules, also three-parameter potentials have been shown to give better results than the two-parameter ones (STEELE[17]). Also, wide preference has been given to three-parameter potentials for non-ionic potentials. It is always desirable to improve two-parameter potentials by suitably introduced three parameters.

One may feel that the real test of the three-parameter potential is whether it can produce the higher order constants such as γ_e, β_e etc. However, it has been pointed out earlier that in the spirit of the Dunham method it is not possible to get higher order spectroscopic constants for alkali halides with any potential function. Since in a potential function for alkali halides we have to take into account the highly ionic character of the bond which varies with increasing internuclear distance, it is not in principle possible to get satisfactory values of higher order spectroscopic constants of alkali halides (VARSHNI and SHUKLA[18], KLEMPERER and RICE[16]). Hence a presently available test for three-parameter potential functions is to calculate $\omega_e x_e$ values which contribute more to the eigenvalues than the higher order constants.

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